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OFFICE OF
CHEMICAL SAFETY AND
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MEMORANDUM

Subject: *d*-Limonene: Ecological Risk Assessment for Registration Review

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This memorandum transmits the Environmental Fate and Effects Division's (EFED) ecological risk assessment for *d*-limonene. The results of this screening-level risk assessment indicate:

For broadcast/directed spray applications of *d*-limonene:

- The major risk concerns are for potential effects to terrestrial invertebrates. Although there are no toxicity data to derive risk quotients, risk is assumed based on the fact that this pesticide is registered for use as an insecticide.

- The level of concern is also exceeded for non-target plants inhabiting areas near the treated field (*i.e.,* within 15 feet).

- Acute and chronic risk has been identified for mammals. Although this chemical is practically non-toxic to mammals, the risk identified in this assessment can be attributed to very high application rates (*i.e.,* up to 55 lb a.i./A).

- Effects are not expected for birds (and reptiles) at the lower rates modelled and risks are uncertain at the higher rates (*e.g.,* 34 and 55 lb a.i./A). Risk to birds on a chronic exposure basis is also uncertain due to a lack of data.

- Effects are not expected for fish, amphibians, aquatic invertebrates and plants.

For small scale applications of *d*-limonene (aerosol spray, crack and crevice, etc.):

- Effects to mammals, birds, plants and aquatic animals are not expected

- Effects to terrestrial invertebrates are of concern.

At this time, there have been no data submitted to assess the risk to pollinators. *d*-limonene is registered for use as an insecticide and is generally applied via foliar applications, thus, data are needed in order to conduct an assessment for pollinators; namely, bees. The following studies are recommended to support this assessment.

These studies include:

1. Honey Bee Adult Acute Contact Toxicity (Guideline 850.3020)
2. Acute oral toxicity to adult honey bees (Non-guideline, OECD TG 213)
3. Acute oral toxicity to larval honey bees (Non-guideline, OECD TG 237)
4. Chronic oral toxicity to adult honey bees (Non-guideline)
5. Chronic oral toxicity to larval honey bees (Non-guideline)
6. Honey bee toxicity of residues on foliage (Guideline 850.3030)
7. Field trial of residues in pollen and nectar (Non-guideline)
8. Semi-field testing for pollinator (Non-guideline, OECD Guidance 75)
9. Field testing for pollinators (Guideline 850.3040)

I. EXECUTIVE SUMMARY

A. Nature of the Stressor

Limonene (*d*-limonene) [(4*R*)-1-methyl-4-(1-methylethenyl)cyclohexene; CAS No, 5989-27-5] is a naturally occurring chemical obtained from the rind of citrus fruits. Limonene is a hydrocarbon classified as a cyclic terpene. The chemical exists as two optical isomers, *d*- and *l*-limonene, and the *d/l*-racemic mixture. The limonene enantiomer, or active ingredient (a.i.) under review is the *d*-enantiomer (i.e., the dextrorotatory enantiomer). This dextrorotatory enantiomer has the *R*-absolute configuration. In this assessment, unless otherwise specified, the term "limonene" is used interchangeably with "*d*-limonene."

d-limonene is used as an acaricide, herbicide, insecticide, and also as an insect repellent/feeding depressant. There are a variety of uses registered including: agricultural crops (citrus, pome fruits, grapes, etc.), ornamental plants, Christmas tree plantations, fencerows, recreational areas, wood protection, and many indoor uses (see Appendix 1 for a comprehensive listing of the types of registered uses). Limonene is not applied aerially. Limonene can be applied using sprayers (ready-to-use containers, hooded sprayers, pump sprayers, pressurized containers), aerosol containers (cans), impregnated strips, injection equipment or with a sponge. The labels for the *d*-limonene registrations suggest a wide range of potential treatment areas [*i.e.,* spot treatment (ft^2) to crops (acres)]. With applications such as spot treatments or edge/perimeter treatments, the application rates used in the exposure models often lead to uncertainty in the exposure estimates (*e.g.,* scaling spot treatment applications up to an acre). The maximum number of applications and maximum yearly application rate, and reapplication interval are also not specified for many registrations (labels).

There is a wide range of application rates when a treatment area is specified with rates that range from 4.6 to 55.2 lb a.i./A per application for treating ornamentals and for herbicidal use in agricultural crops. The maximum yearly rate is 415.2 lb a.i./A/yr.

The insecticidal mode of action of limonene is believed to be similar to pyrethrum - by affecting the sensory nerves of the peripheral nervous system (not a cholinesterase inhibitor)[1]. As an herbicide, *d*-limonene is a non-systemic, contact herbicide that strips the waxy rind or cuticle from plants, causing death of the plant by desiccation[2].

The major route of dissipation for *d*-limonene is volatilization. Other dissipation processes include photodegradation in air, microbial-mediated aerobic soil metabolism, sorption to soil, and transport in runoff water. Limonene is stable to hydrolysis. The vapor pressure (2 mm Hg @ 20˚C) and Henry's Law Constant (2.6×10^{-2} atm-m^3/mole) indicates that limonene is highly volatile and that it will readily volatilize from soil and water. However, this dissipation process competes with binding. Limonene binds strongly to soil (K_{oc} > 1000 mL/g_{oc}), therefore it is

[1] Ware, G.W. and Whitacre, D.M. 2004. The Pesticide Book. 6th Edition. Pg. 66
[2] Stephen O. Duke, Joanne G. Romagni, Franck E. Dayan 2000. Natural products as sources for new mechanisms of herbicidal action. Crop Protection 19 (2000) 583-589.

expected to be relatively immobile in soils. Because aerobic metabolism studies have not been submitted for *d*-limonene, published aerobic biodegradation studies were used to estimate a first order biotransformation rate with a half-life of 38.5 days. Under anaerobic conditions, *d*-limonene appears to be persistent.

B. Summary of Effects and Risk Conclusions

For broadcast/directed spray applications of *d*-limonene:

- The major risk concerns are for potential effects to terrestrial invertebrates. Although there are no toxicity data to derive risk quotients, risk is assumed based on the fact that this pesticide is registered for use as an insecticide.
- The level of concern is also exceeded for non-target plants inhabiting areas near the treated field (*i.e.,* within 15 feet).
- Acute and chronic risk has been identified for mammals. Although this chemical is practically non-toxic to mammals, the risk identified in this assessment can be attributed to very high application rates (*i.e.,* up to 55 lb a.i./A).
- Effects are not expected for birds (and reptiles) at the lower rates modelled and risks are uncertain at the higher rates (*e.g.,* 34 and 55 lb a.i./A). Risk to birds on a chronic exposure basis is also uncertain due to a lack of data.
- Effects are not expected for fish, amphibians, aquatic invertebrates and plants.

For small scale applications of *d*-limonene (aerosol spray, crack and crevice, etc.):

- Effects to mammals, birds, plants and aquatic animals are not expected
- Effects to terrestrial invertebrates are of concern.

II. PROBLEM FORMULATION

A. Pesticide Type, Class, and Mode of Action

Limonene (*d*-limonene) [(4*R*)-1-methyl-4-(1-methylethenyl)cyclohexene; CAS No, 5989-27-5] is a naturally occurring chemical obtained from the rind of citrus fruits. Limonene is a hydrocarbon classified as a cyclic terpene. Specifically, it is a monoterpene. Limonene has a chiral (stereogenic) carbon. Thus, limonene occurs as an enantiomeric pair (i.e., as two non-superimposable mirror-image chemical structures and therefore, each enantiomer is optically active[3]. The structure of *d*-limonene is shown in Figure 1. The limonene enantiomer under review is the *d*-enantiomer (i.e., the dextrorotatory enantiomer). This dextrorotatory enantiomer has the *R*-absolute configuration. In this assessment, unless otherwise specified, the term "limonene" is used interchangeably with "*d*-limonene."

[3] The chirality of limonene arises from an asymmetric carbon atom (i.e., carbon is the chiral/stereogenic center). The odors of *l*-limonene and *d*-limonene are different; *l*-limonene smells piney and turpentine like and d-limonene has a pleasing orange scent. This is associated with enantiomer-specific interactions with chiral olfactory receptors.

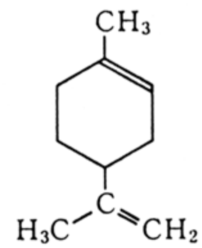

Figure 1. Structure of *d*-Limonene

The insecticidal mode of action of limonene is believed to be similar to pyrethrum - by affecting the sensory nerves of the peripheral nervous system (not a cholinesterase inhibitor)[4]. As an herbicide, *d*- limonene is a non-systemic, contact herbicide that strips the waxy rind or cuticle from plants, causing the plant to desiccate, resulting in the death of the plant[5].

The major route of dissipation for *d*-limonene is volatilization. Other dissipation processes include photodegradation in air, microbial-mediated aerobic soil metabolism, sorption to soil (*e.g*., organic carbon), and transport in runoff water (IPCS, 1998[6]). Functional groups of limonene, cyclohexane ring and ethylene group, are not prone to hydrolysis. Microbial mediated degradation is an important degradation pathway. Degradation rates in aerobic sewage sludge have been reported to range from 41-98% degradation in 14 days to >93% degradation in 14 days. Biotic degradation of limonene has been observed with some specific microorganisms. These studies were not designed to determine the biodegradation rates of limonene, but suggested that limonene biodegradation (biodegradability in aerobic aqueous medium, OECD, 1992[7]) was occurring as the biochemical oxygen demand ranged from 41 to 98% in 14 days (IPCS, 1998). Because aerobic metabolism studies have not been submitted for *d*-limonene, published aerobic biodegradation studies were used to estimate a first order biotransformation rate (d^{-1}); for a half-life of 38.5 days[8,9] (Appendix 2). Under anaerobic conditions, *d*-limonene appears to be persistent. In the atmosphere *d*-limonene will photo-chemically degrade producing hydroxyl and nitrate radicals and ozone.

B.Overview of Pesticide Use and Usage

The production of *d*-limonene and use in flavorings, fragrances, cosmetics, as a solvent, a wetting agent, and in the manufacture of resins may result in its release to the environment through various waste streams. *d*-limonene is also found in many oils and fruits and is emitted to the environment from plants and the combustion of wood. *d*-limonene is used as both an active

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[5] Ware, G.W. and Whitacre, D.M. 2004. The Pesticide Book. Pg. 66

[5] Stephen O. Duke, Joanne G. Romagni, Franck E. Dayan 2000. Natural products as sources for new mechanisms of herbicidal action. Crop Protection 19 (2000) 583-589.

[6] IPCS, 1998. http://www.inchem.org/documents/cicads/cicads/cicad05.htm

[7] OCED, 1992. http://www.oecd.org/chemicalsafety/risk-assessment/1948209.pdf

[8] Misra, G. and Pavlostathis, S.G., 1997. Biodegradation of monoterpenes in liquid and soil-slurry systems. Appl. Microbiol. Biotech. 47:572-577.

[9] Rifai, H.S. and C.J. Newell. 1998. Estimating First-Order Decay Rates for BTEX Using Data from 115 Sites, in *Proceedings* of the 1998 NGWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, Nov. 11 - 13, Houston, Texas, pp. 31 – 41, National Ground Water Association, Westerville, OH.

and inert ingredient in pesticide formulations. *d*-limonene is used as an acaricide, herbicide, insecticide, and insect repellent/feeding depressant. Formulations include an emulsifiable concentrate, impregnated material, pressurized liquid, and a ready-to-use liquid. A summary of use sites is shown in Table 1.

Table 1. Summary of Use Sites Registered for *d*-limonene

Use Sites	Groups
Terrestrial	Citrus fruits, cole crops, flavoring/spice crops, fruiting vegetables, grapes, leafy vegetables, legume vegetables, pome fruits, root and tuber vegetables, small fruits, tree nuts, Christmas trees; Nursery stock; Ornamentals (plants, trees, turf); Outdoor buildings and structures(perimeter); sidewalks, rights-of-ways/fencerows/hedgerows; Refuse/solid waste sites/Manure; Recreational Areas; Sewage systems; Wood protection treatment to buildings/products
Indoor	Household/domestic dwellings Commercial/institutional/industrial premises/vehicles Dogs/ Cats; Pet living/sleeping quarters Human body-clothing while being worn Wide area general indoor treatment (public health) Wood protection treatment to buildings/products

Limonene is not applied aerially. It is applied using ground sprayers (ready-to-use containers, hooded sprayers, pump sprayers, and pressurized containers), aerosol containers (cans), impregnated strips, injection equipment, or manually with a sponge. There is a wide range of limonene concentrations and application rates for the formulated products. Because many of the uses are “spot” treatments or edge or boundary use, the application rates used in the exposure models lead to uncertainty.

Many of the labels for *d*-limonene do not provide a complete application rate (e.g., the label may say to spray for 10 seconds or only states a concentration in lb/gal without a finish spray volume). Current models used by EFED to estimate exposure require application rates on a per unit area basis (*e.g.,* lb a.i./A). Other label issues are the lack of a maximum yearly (or seasonal) rate, the number of applications per year, or the reapplication interval. Additionally, because of the large range in rates, this assessment has focused on the labels with the highest application rates.

The aquatic exposure assessment is focused on the Avenger™ AG Burndown Herbicide (EPA Reg. No. 82052-4) and the Orange Guard Ornamental Plants Protection Concentrate (EPA Reg. No. 61887-3) products, both of which specify the application rates on a per area basis. With single application rates as high as 34.6 lb a.i./A for the Avenger™ AG Burndown Herbicide and 55.2 lb a.i./A for the insecticide Orange Guard Ornamental Plants Protection Concentrate, these products provide an upper-bound screen for aquatic exposures. The burndown herbicide product can be applied to a variety of agricultural crops as a broadcast or spot treatment with ground equipment such as a directed sprayer or hooded sprayer. When the application rate of

34.6 lb a.i./A is used, the herbicide is applied as a spray over the target vegetation. The label does not specify a maximum number of applications or a yearly application rate. However, additional information was provided to clarify the intended use indicating a maximum of 12 applications with a 2-day minimum reapplication interval[10]. Literature suggests that repeat applications may be necessary for larger weeds.[11,12,13] The Orange Guard product is intended for use as a foliar (insecticide) spray to protect ornamental plants and when factoring in the high finished spray volumes, the rates are as high as 55.2 lb a.i./A (with up to six applications/yr at a 7-day interval).

For the terrestrial exposure assessment, additional scenarios were selected to bound the potential exposures to terrestrial organisms. Thus, in addition to the scenarios discussed above, the lower rates on the Orange Guard label (4.6 and 18.4 lb a.i./A) were also quantitatively assessed. These additional scenarios also bracket the non-broadcast labeled uses such as the perimeter treatment, mound sprays and spot treatments with rates such as 0.454 lb a.i./sq ft (19.79 lb /A for moss and algae control on lawns) and 0.2265 lb a.i./mound (assuming 40 mounds/A = 9.06 lb a.i./A). While these "per acre" extrapolations are high, they are the values that would be used in the TREX model to estimate the residues on feed items within the spot/area treatment that the animal may be foraging.

Given the low toxicity of *d*-limonene, the small scale applications (aerosol spray, crack and crevice, etc.), were not quantitatively assessed in this assessment. Table 2 provides an overview of the uses that are considered representative of the highest use patterns. The application rates in bold were selected for exposure modeling. For a complete list of all *d*-limonene uses see Appendix 1.

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[10] Correspondence from S. McIntosh to R. Wasem (April 11, 2014).
[11] http://ucanr.edu/blogs/blogcore/postdetail.cfm?postnum=6498
[12] http://www.groworganic.com/avenger-weed-killer-conc-32-oz.html
[13] http://avengerorganics.com/LinkClick.aspx?fileticket=sWUA%2BS%2BCs6g%3D&tabid=81

Table 2. Overview of Representative High Exposure *d*-limonene Uses

Crop/Site	Product/ Reg. number	Timing; App. Type	Method/ Equipment	Maximum Single Application Rate (lb a.i./A)	Max Rate Per Year lb a.i./A	Max. Num. Apps. /Yr	MRI (d)	Comments
Ornamental plants in greenhouses, nurseries, Christmas tree plantations, and landscapes (residential commercial, industrial)	Orange Guard-Ornamental Plants (5.8%) Insecticide/ Repellent 61887-3	Foliar Broadcast	Ground Sprayer/Pump sprayer/ Handheld	**4.6**	27.6	6	7	Rates were expressed as dilution of (1:4; 0.092 lb a.i./gal water), or (1:6) with various finish spray volumes. "row crops 25-50 gal/A; vine crops 50-200 gal/A, tree crops 100-400 gal/A, greenhouse 100 gal /10,000 sq ft, 600 gal per A-forestry".
				18.4	110.4			
				36.8	220.8			
				40.1	240.6			
				55.2	331.2			
Ag. Crops: Brassica veg; citrus; grapes; herbs; leafy veg; legume veg; pome fruit; root & tuber veg; small fruit; stone fruit; tree nuts	Avenger™ AG Burndown herbicide (55%) 82052-4[a]	Weed post-emergence/ burndown Broadcast and Spot treatment	Ground Sprayer-Directed /Hooded sprayer	**34.6**	415.2	12[b]	2[b]	Label states do not exceed 8.5 gallons of product per acre per application (4.07 lb a.i./gal * 8.5 gal/A= 34.60 lb a.i./A).
Borders around driveways, patios, sidewalks, mature trees and ornamentals, buildings, residential greenhouses, fencerows, flowerbeds	Avenger Weed Killer Conc. (70%)/ RTU (17.5%) 82052-1 82052-3	Weed post-emergence/ burndown Perimeter/ Spot	Ground Sprayer	1.28-1.47 lb a.i./gal (dilution) 51-59 lb a.i./A*	NS	12[b]	2[b]	*Assumed 40 gallons per A because the label did not have a finish spray volume to complete the rate. Need further clarification on label to reduce uncertainty. Given the uncertainty and the use as perimeter/spot treatment, this assessment will use the high scenarios above to inform on the risk for this use.

[a] Label provides sprayer requirements: Do not use nozzles or nozzle configurations which produce fine droplets (mist). Use low drift, low pressure nozzles and spray hoods must operate on the ground or skimming across ground surface

[b] The minimum retreatment interval was not specified on the label but the registrant suggested every 2 days for difficult to treat weeds.

Limonene Usage

National-level pesticide usage data for *d*-limonene is not available. *d*-limonene usage data has been reported by the California Department of Pesticide Regulation Pesticide Use Reporting and was summarized by USEPA's Biological and Economic Analysis Division (BEAD) (**Table 3**).

Table 3. Limonene Usage Data: California, 2001-2012

Year	Pounds A.I. Applied *(Ag[a] & Non Ag[b] Applications)*	Cumulative Acres Treated *(Ag Only)*
2001	40,703	34,695
2002	37,393	39,562
2003	28,072	48,939
2004	14,349	49,320
2005	45,877	62,359
2006	32,843	75,333
2007	68,949	79,012
2008	45,536	64,151
2009	56,495	55,465
2010	56,403	29,621
2011	14,460	10,025
2012	17,976	73,328
AVG	42,662	51,818

Source: California DPR, 2010, Summary of Pesticide Use Report Data, Use Trends of Biopesticide Pesticides: http://www.cdpr.ca.gov/docs/pur/pur10rep/10sum.htm

C. Previous Ecological Risk Assessments and Evaluations

The ecological risk assessment for the Reregistration Eligibility Decision (RED), completed in September 1994 (EPA 738-R-94-034), was based on a limited number of environmental fate and ecological toxicity studies. Exposure concentrations for the risk assessment were estimated using simple screening level exposure models and limited toxicity data. The risk assessment concluded that minimal risk is anticipated for birds, mammals, and aquatic animals for the pesticidal uses of limonene. EFED believed at that time that applications of limonene did not pose any undue risks to endangered species. The 1994 assessment prepared for the RED did not include a terrestrial or aquatic plant assessment because limonene was not registered as an herbicide at that time. Additionally, several new uses have been registered (for example, the Burndown Herbicide-Avenger™ AG) so the rates in this current assessment are substantially higher than previous assessments. Additional ecological data for plants (terrestrial and aquatic) have also been submitted and considered in this assessment along with additional mammal data that was cited in the 2007 TRED (the previous assessment was based on a non-definitive acute oral endpoint and did not consider any chronic data).

Although, no additional environmental fate data has been submitted, published literature was reviewed and used to confirm previously used values or change or add an additional value (*e.g.*, degradation or dissipation process), if appropriate. The Food and Drug Administration (FDA) considers limonene to be Generally Recognized as Safe (GRAS) as a food additive when used as a synthetic flavoring substance and adjuvant (21 CFR §182.60).

III. Risk Hypothesis and Conceptual Model

A. Measures to Evaluate Risk Hypotheses

In the case of *d*-limonene, measures of exposure are based on terrestrial and aquatic exposure models[14] that estimated environmental concentrations (EEC) of *d*-limonene using maximum labeled application rates. The T-REX model (version 1.5.2) was used to produce terrestrial EECs on wildlife food items. The STIR model was not used in this assessment because inhalation toxicity data were not available. The TerrPlant and AgDRIFT models are used to estimate exposure to nontarget plants. The Surface Water Concentration Calculator (SWCC[15]; version 1.106) (see Section III A. 1) and the linked PRZM/EXAMS with PE5[16] are used to produce aquatic EECs and drinking water EDWCs. Because the SWCC currently does not include volatilization from soil, whereas PRZM does, aquatic exposure (EECs) concentrations were refined with PRZM/EXAMS for the scenarios that resulted in the highest concentrations estimated by SWCC. Both consider volatilization from water. Limited monitoring data for air and water are available, but these data were collected in studies that were not specifically targeted for the pesticidal uses of limonene.

Measures of effect are obtained from a suite of studies conducted with a limited number of surrogate species. The lowest toxicity endpoints for the most sensitive surrogate test species are used to estimate treatment-related effects on growth, reproduction and/or survival.

B. Risk Hypothesis

For this assessment, the risk to non-target organisms is based on potential effects from the application of *d*-limonene to the environment. The Agency presumes the following risk hypothesis for this screening level assessment:

> *Based on mode of action, the proposed use patterns, and the sensitivity of non-target aquatic and terrestrial species, the proposed uses of d-*limonene *have the potential to reduce survival, reproduction, and/or growth in terrestrial and aquatic animals and plants through direct application, spray drift and/or runoff.*

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[14] http://www.epa.gov/pesticides/science/models_pg.htm
[15] http://www.epa.gov/oppefed1/models/water/index.htm#swcc
[16] PE5 suite of models (PE5 v5.0, PRZM v3.12.2, EXAMS v2.98.04.06) and scenarios

In order for a chemical to pose an ecological risk, it must reach non-target organisms at concentrations found to cause adverse effects. The assessment of ecological exposure pathways in this assessment includes an examination of the source and potential migration pathways to *d*-limonene exposure, and the determination of potential adverse effects on non-target species.

C. Conceptual Model

Application methods for *d*-limonene involve foliar spray via ground equipment. Ecological receptors that may potentially be exposed to *d*-limonene include terrestrial and semi-aquatic wildlife (*i.e.*, mammals, birds, amphibians, terrestrial invertebrates, and reptiles) and plants. In addition, aquatic receptors (*e.g*., freshwater and estuarine/marine fish and invertebrates, amphibians, and plants) may also be exposed as a result of potential movement of *d*-limonene via spray drift and/or runoff from the site of application to aquatic environments. Exposure to terrestrial animals is based primarily on dietary consumption of foliar residues while aquatic assessments assume that all major potential routes of direct exposure are accounted for. The major transport pathway for *d*-limonene is volatilization.

IV. Measures of Exposure

Limonene functions as an acaricide, herbicide (including moss and algae pests in terrestrial environments), and also as an insecticide/repellent. The insecticide/repellent uses tend to be more of a spot treatment in nature, whereas the herbicide uses can include spot treatment, perimeter/border treatment, or treatments to a field (although the applications are generally directed applications rather than full-acre broadcast treatments).

The environmental fate data for this assessment was generally obtained from open literature data such as the World Health Organization (IPCS, 1998[17]) and Limonene (CICAD#5, 1998[18]), TOXNET (2006[19]) and USEPA High Production Volume Information System (HPVIS), 2014[20] and are essentially the same as the previous assessment conducted for the RED. These sources generally report the same information because they tend to cross-reference each other. Data values from these sources were generally selected to be consistent with the RED (1994) and the USEPA OPPT Screening Level Hazard Characterization of Monoterpene Hydrocarbon Category.[21,22] Additional information was included when available. Chemical identification and physical-chemical properties of limonene are shown in **Table 4**. When available, experimental physical-chemical properties are reported. Exposure concentrations were estimated using simple screening level exposure models.

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[17] IPCS, 1998. http://www.inchem.org/documents/cicads/cicads/cicad05.htm
[18] CICAD#5, 1998. http://whqlibdoc.who.int/publications/1998/9241530057.pdf
[19] TOXNET, 2006. http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1809
[20] http://www.epa.gov/chemrtk/hpvis/hazchar/Category%20Monoterpenes_Sept2009.pdf
[21] http://www.epa.gov/hpvis/hazchar/Category%20Monoterpenes_Sept2009.pdf
[22] http://ofmpub.epa.gov/oppthpv/quicksearch.display?pChem=101509

A. Environmental Fate and Modeling Input Parameters

Physical/Chemical and Environmental Fate Properties

The physical/chemical properties and environmental fate properties of *d*-limonene are listed in Table 4.

Table 4. Identity and Physical-Chemical Properties of *d*-limonene

Type of Information	Information	Source
Chemical name	IUPAC: (*R*)-4-isopropenyl-1-methylcyclohexene or *p*-mentha-1,8-diene CAS (4*R*)-1-methyl-4-(1-methylethenyl)cyclohexene	http://www.alanwood.net/pesticides/d-limonene.html
Pesticide type	Acaricide, herbicide, insecticide, repellent/feeding depressant	Pesticide Labels
CAS Reg. No.	*d*- limonene: 5989-27-5 Racemate: 7705-14-8 *l*- Limonene: 5989-54-8	http://www.alanwood.net/pesticides/d-limonene.html
Empirical Formula	$C_{10}H_{16}$	http://www.alanwood.net/pesticides/d-limonene.html
Smiles String	C(=CCC(C(=C)C)C1)(C1)C	
Molecular mass (g/mol)	136.23	CICAD#5, 1998; IPCS, 1998
Physical State	Liquid (colorless)	CICAD#5, 1998; IPCS, 1998
Specific gravity	0.8411 g/cm^3 (7.4 lb/gallon)	CICAD#5, 1998; IPCS, 1998
Melting point ˚C	-74.35	CICAD#5, 1998; IPCS, 1998 HPVIS, 2014
Boiling point ˚C	175.5-178.6 @ 760 mm Hg 176 @ 760 mm Hg	CICAD#5, 1998; WHO, 1998 HPVIS, 2014[a]
Solubility in water (mg/L)	13.8 @ 25˚C	Massaldi and King, 1973[23]. [*J. Chem. Eng. Data*, 1973, *18*:393-397] CICAD #5, 1998; IPCS, 1998 HPVIS, 2014
Vapor pressure	1 mm Hg @ 20˚C 2 mm Hg @ 20˚C 3 mm Hg @ 14.4 ˚C 1.43 mm Hg @ 20˚C (measured) 1.2 mm Hg @ 20˚C 1.59 mm Hg @ 20˚C	MRID 93136002 MRID #46511103 (Product Chemistry) EPA HQ-OPP-2004-0335-003.pdf IPCS, 1998; HPVIS, 2014 HPVIS, 2014 FFHPVC Terpene Consortium[b,]
Henry's Law Constant (calculated)	1.3 x 10^{-2} atm-m^3/mole @ 20˚C [1 mm Hg] 1.8 x 10^{-2} atm-m^3/mole @ 20˚C [1.43 mm Hg]	(Solubility – 13.8 mg/L) Copolovici and Niiements, 2005

[23] http://pubs.acs.org/doi/pdf/10.1021/je60059a024

Type of Information	Information	Source
	2.6 x 10^{-2} atm-m^3/mole @ 20˚C [2 mm Hg] 2.8 x 10^{-2} atm-m^3/mole @ 20˚C 2.8 x 10^{-2} atm-m^3/mole @ 25˚C 3.2 x 10^{-2} atm-m^3/mole	SRC as cited by TOXNET, 2006
Enthalpy of Vaporization	kj/mole (kcal/mole) 37.8 (9.03) to 49.9 (11.93)	Chickos J.S. and Acree, W.E. 2003..J. Phys. Chem. Ref. Data. 32:519-877. http://www.chemicaldictionary.org/dic/D/D-Limonene_332.html Clará et al. 2009. J. Chem. Eng. Data 54:1087-1090. Copolovici and Niiements, 2005
Organic Carbon Partition Coefficient (K_{oc}) (mL/g_{oc})	1,300 1,030 to 4,780 (estimated) 1,260 (estimated)	TOXNET, 2006; CICAD#5, 1998; IPCS, 1998; 1030 HPVIS, 2014
Log K_{ow} (*n*-octanol/water partition coefficient)	4.88; 4.83 @ 25˚C (calculated) 4.23 @ 20˚C (measured) 4.50 @ 25ºC	CICAD#5, 1998; IPCS, 1998; HPVIS, 2014. Copolovici and Niiements, 2005
Log $K_{o\text{-}air}$ (octanol-air partition coefficient)	4.26	(estimated; EPISuite)
pK_a/pK_b	Not applicable	-
Bioconcentration Factor (BCF)	246 to 262 (estimated from log Kow 4.23) 660 (estimate from log Kow 4.57)	CICAD#5 TOXNET, 2006
Aqueous Photolysis Half-life [$t_{½}$](days)	0.037 days (reported as 0.884 hours)	HPVIS, 2014 FFHPVC Terpene Consortium[b,c] Estimated, AOPWIN, EPI Suite 2000
Foliar Dissipation Rate	Estimated 2.79 to 4.67 ppm/hour	MRID 47548301

[a] HPVIS, 2014. High Volume Information System: http://www.epa.gov/chemrtk/hpvis/hazchar/Category%20Monoterpenes_Sept2009.pdf
[b] http://ofmpub.epa.gov/oppthpv/document_api.download?FILE=Summaries%20sn133.pdf
[c] http://www.epa.gov/hpv/pubs/summaries/monoterp/c13756rt.pdf

Environmental Fate/Exposure Summary

Much of the physicochemical and environmental fate values for *d*-limonene are based upon values reported in literature and were estimated by models such as EPI (Estimate Program Interface) Suite[24] and were obtained from a variety of published sources (CICAD #5, 1998; TOXNET, 2006; HPVIS, 2014; SRC, 2014; IPCS, 1998). While there is variability in the values reported in literature, the conclusion derived in this assessment would be the same (low solubility, volatile, low mobility in soil, photodegradable in air, and biodegradable under aerobic conditions) (Clará et al., 2009; Copolovici and Niinemets, 2005). Also, some of the measured data may actually be the *d/l*-limonene (racemic mixture) rather than *d*-enantiomer (*i.e.*, *d*-limonene). Where values are available both for the *d*- and *d/l*-limonene, they are generally similar in order

[24] EPI Suite,2014 http://www.epa.gov/opptintr/exposure/pubs/episuite.htm

of magnitude. The routes of dissipation for *d*-limonene include volatilization, photodegradation in air, microbial-mediated aerobic soil metabolism, and binding to soil/sediment (IPCS, 1998; TOXNET, 2006).

Limonene is stable to hydrolysis. Microbial mediated degradation is an important degradation pathway as biotic degradation of limonene has been observed with some microorganisms in some pure microbial cultures[25]. Degradation in aerobic sewage sludge has been reported to range from 41-98% degradation in 14 days. These studies were not designed to determine the biodegradation rates of limonene, but suggested that limonene biodegradation (biodegradability in aerobic aqueous medium, OECD, 1992[26]) was occurring as the biochemical oxygen demand ranged from 41 to 98% in 14 days. Because aerobic metabolism studies have not been submitted for *d*-limonene, published aerobic biodegradation studies were used to estimate a first order biotransformation rate for the *d*-limonene; resulting in a half-life of 38.5 days[27,28] (Appendix 2). Under anaerobic conditions, *d*-limonene appears to be persistent.

In the atmosphere, volatilized limonene undergoes rapid bi-molecular gas-phase reactions with ozone, nitrate radicals, and photochemically generated hydroxyl radicals. Volatilization half-lives from water were estimated to range from 1 hour to 5 days, for a river and a lake model, respectively (TOXNET, 2006). Photodegradation in air of *d*-limonene is an important degradation pathway in the atmosphere. Degradation mechanisms have been associated with hydroxyl radicals ($t_{1/2}$=0.32 to 2 hours), ozone ($t_{1/2}$=0.18 to 2.6 hours), and nitrite radicals ($t_{1/2}$=0.08 to 0.015 hours) (TOXNET, 2006). Photodegradation products in air are: hydroxyl radical degradation products including 4-acetyl-1-methylcyclohexane, a ketoaldehyde, formaldehyde, 3-oxobutanal, glyoxal, and C10 dicarbonyl; ozonolysis degradation products including bis(hydroxymethyl)peroxide, hydrogen peroxide; and nitrite radical degradation products include formaldehyde, acetaldehyde, formic acid, acetone, and prooxyacetyl nitrate.

A study [MRID 47648301] was submitted for QRD 400/QRD 416 for a residue trials for mustard greens. QRD 400 (total 18.5% a.i.) and QRD 416 (total 17.43% a.i.) contain a mixture of 3 active ingredients terpenes *α*-terpinene, *ρ*-cymene, and *d*-limonene. The two products were applied to mustard green foliage at a rate of 2.6 and 2.4 lb a.i./A for QRD 400 and QRD 416, respectively. Leaves were harvested at 0-, 1-, and 4- hours. *d*-limonene levels generally dropped below the limit of quantification (LOQ=0.05 ppm) at 1-hour. Although, a half-life could not be determined, the rate of decline for *d*-limonene ranged from 2.8 to 4.67^{-hr}. Adjusting the 2.4 or 2.6 lb a.i./A to the maximum rate for d-limonene (34.6 lb a.i./A), the time required for the *d*-limonene concentrations to drop below the LOQ ranged between 3 and 15 hours (Table 4).

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[25] Amaral, J.A., Keins, A., Richards, S.R., and Knowles, R. 1998. Effect of Selected Monoterpenes on Methane Oxidation, Denitrification, and Aerobic Metabolism by Bacteria in Pure Culture. Applied and Environmental Microbiology, Vol 64(2), pp 520-525.

[26] OCED, 1992. http://www.oecd.org/chemicalsafety/risk-assessment/1948209.pdf

[27] Misra and Pavlostathis. 1997. Appl. Microbiol. Biotechnol. 47:572-577.

[28] Rifai and Newell, 1998. https://info.ngwa.org/GWOL/pdf/982664575.PDF

The estimates of soil organic carbon partitioning coefficient (K_{oc}) for *d*-limonene ranged between 1,030 and 4,780 mL/g_{oc} (SRC, 2014; CICAD#5, 1998, WHO, 1998). Based on the FOA mobility classification, *d*-limonene is expected to be slightly mobile in soil[29]. It would tend to bind to eroded soil and be transported in runoff water. However, the high vapor pressure (1 to 3 mm Hg) and calculated Henry's Law Constants ranged between 1.3 x 10^{-2} and 3.2 x 10^{-2} atm-m^3/mole, depending upon the vapor pressure value and solubility (7.54 to 13.8 mg/L), indicate that limonene will readily volatilize from soil and water (Table 4). However, this dissipation process competes with binding.

The estimated log octanol-water partition coefficients (K_{ow}s) range from 4.23 to 4.83 indicates potential bioaccumulation. However, the bioconcentration factor, calculated on the basis of water solubility and the log octanol/water partition coefficient, ranged 246 to 262 suggesting that limonene is not expected to bioaccumulate in fish and other aquatic organisms. TOXNET (2006) gives an estimated BCF value of 660. A log Kow between 4 and 8, would typically trigger use of the KABAM model to determine if there are food chain concerns for birds and mammals from consuming aquatic organisms with accumulated residues, however, because of the low BCF values, the high Henry's Law Constant showing high volatility from water, and low/non-definitive toxicity for birds and mammals, this analysis was not conducted.

Monitoring Data Detections in Environmental Media

Limonene residues have been detected in rural, urban, suburban, and forest areas in the U.S. and in other countries. These residues have been detected in air, surface water, ground water, seawater, wastewater, ice, soils, and in solid waste composting facilities. Levels of limonene are varied, but the limited data do not allow for a correlation with usage or geographical region.

The National Water Quality Assessment Program (NAWQA, 2014) database for *d*-limonene reports 481 samples collected in ambient surface of water, 602 groundwater samples, and 296 treated water supplies. The limit of detection appears to range from 0.013 to 0.5 µg/L). The maximum concentration was 1.2, 0.072 and 0.157 µg/L, in surface water, groundwater, and treated water supplies, respectively. These monitoring studies were not targeted and many were conducted prior to the registration of Avenger[TM] Burndown pesticide (EPA. Reg No. 82052-4). The CICID#5 (1998) and TOXNET (2006) reported (Table 5) detections observed in a number of media from other studies. The detections of limonene (or *d*-limonene) in these monitoring studies may reflect sources other than pesticidal use (*i.e*., sewage treatment).

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[29] USEPA. 2006. *Standard Soil Mobility Classification Guidance.* Memorandum From S. Bradbury to Environmental Fate and Effects Division. April 21, 2006. Environmental Fate and Effects Division. Office of Pesticide Programs. United States Environmental Protection Agency.

Table 5. Concentrations of Limonene (or d-limonene) observed in monitoring studies collected from various media.

Medium	Concentration	Source
Outdoor Air	0.036 to 32 μg/m^3	CICAD#5, 1998
Lake Water	0.47 to 84 ng/L	CICAD#5, 1998
Drinking Water	Max. 30 ng/L (5 of 14 samples) Max. 1.87 x 10^5 ng/L (1 of 182 samples	CICAD#5, 1998
Estuary	25 to 633 ng/L	CICAD#5, 1998
River Water	590 to 1,600 ng/L	CICAD#5, 1998
Sea Water	2 to 40 ng/L	CICAD#5, 1998
Ground Water (sewage contaminated)	1,000 to 130,000 ng/L	TOXNET, 2006
Waste Water, Influent, sewage treatment plant	Non-detect to 220,000 ng/L	CICAD#5, 1998
Sediment	105 to 807 ng/kg	CICAD#5, 1998
Ice	4 to 15 ng/L	CICAD#5, 1998
Surface Water	0.013 to 1.2* μg/L (17 of 481)	NAWQA, 2014[30]
Bottom Material	15.4 to 111.1* μg/kg (6 0f 35)	NAWQA, 2014
Groundwater	0.016 and 0.072* μg/L (2 of 602)	NAWQA, 2014
Treated Water Supply	0.028 to 0.157 μg/L (4 of 296)	NAWQA, 2014

* Concentrations are estimated.

Ecological Effects Characterization

There is a limited toxicity data set for *d*-limonene. Tables 6 and 7 summarize the available data for the aquatic and terrestrial taxonomic groups, respectively. The tables provide a preliminary overview of the potential acute toxicity of *d*-limonene by providing the acute toxicity classifications.

Aquatic Organisms

On an acute exposure basis, *d*-limonene is classified as "slightly toxic" to freshwater fish and invertebrates. Data are not available to characterize the effects to aquatic organisms on a chronic exposure basis, or for estuarine/marine animals on an acute basis. For aquatic plants, blue green algae *(Anabaena flos-aquae*) was the most sensitive non-vascular plant with reductions in yield at all test concentrations [blue green algae; EC_{50} = 9.353 mg a.i./L and NOAEC <3.125 mg a.i./L], thus, the EC_{05} (1.731 mg a.i./L) will be used as a proxy for the NOAEC. For non-vascular plants, the EC_{50} and NOAEC were 29.65 and 3.125 mg a.i./L, respectively, based on reductions in frond yield for duckweed (*Lemna gibba*).

[30] http://cida.usgs.gov/nawqa_queries_public/

Table 6. Summary of Aquatic Toxicity Studies for *d*-Limonene

Taxonomic Group	Study Type	Surrogate Species and Test Material	Toxicity Value	MRID and Classification	Acute Toxicity Classification
Freshwater fish	Acute	Rainbow trout *(Oncorhynchus mykiss)*	LC_{50} = 80 mg a.i./L[b]	00146085 (Acceptable)	Slightly toxic
	Chronic	*No Data*			
Freshwater invertebrates	Acute	Water flea *(Daphnia magna)*	EC_{50} = 39 mg a.i./L	00146085 (Acceptable)	Slightly toxic
	Chronic	*No Data*			
Estuarine/ marine fish and invertebrates	*No Data*				
Aquatic plants and algae	Non-vascular	Blue-green algae [a] *(Anabaena flos-aquae)*	EC_{50} = 9.353 mg a.i./L (nominal) *(95% C.I.: 7.4 to 11.8)* NOAEC = <3.125 mg a.i./L EC_{05}=1.731 mg a.i./L Based on reductions in yield	49044004 (Supplemental-quantitative)	N/A
	Vascular	Duckweed (*Lemna gibba*)	EC_{50}=29.65 mg a.i./L (nominal) *(95% C.I.: 19.84 to 44.32)* NOAEC: 3.125 mg a.i./L Based on reductions in frond yield	49044001 (Supplemental-quantitative)	N/A

[a] For non-vascular plants (e.g., algae, diatom), four species were tested and the values from the most sensitive test species are reported.
[b] Exceeds the solubility according to the Fate Section-DER does not mention any precipitate

Terrestrial Organisms

Data are not available to assess the toxicity of *d*-limonene to birds on an acute oral basis. On a sub-acute/dietary exposure basis, *d*-limonene is classified as "practically non-toxic" to birds based on a LC_{50} of >5,600 mg a.i./kg diet and a lack of sublethal effects reported for the Bobwhite quail *(Colinus virginianus*). Data are not available to assess the risk on a chronic exposure basis. For mammals, *d*-limonene is classified as "practically non-toxic" on an acute exposure basis. On a chronic exposure basis, a 2-generation reproductive study was not available so the NOAEL for the rat (250 mg a.i./kg/day) was based on reductions in body weight gain at

500 mg a.i./kg/day treatment level in the available developmental toxicity study. Data are not available to assess the toxicity of d-limonene exposure via inhalation.

For terrestrial invertebrates, there are no toxicity studies available to assess the risk to terrestrial invertebrates. Given that *d*-limonene is registered as an acaricide/insecticide, the acute contact toxicity to the honey bee (*Apis mellifera*) is a data gap.

For terrestrial plants, there were no effects reported in the available seedling emergence study, thus, the NOAEC is ≥265-345 lb a.i./A (MRID 49044005). In the vegetative vigor toxicity study, there were effects reported at all treatment levels so the EC_{05} was used as a proxy for the NOAEC (Monocots- EC_{25}: 2.83 lb a.i./A; EC_{05} = 0.19 lb a.i./A-Dicots EC_{25}=7.09 lb a.i./A; EC_{05} = 1.31 lb a.i./A) which was based on reductions in dry weight (MRID 49098302).

Table 7. Summary of the Terrestrial Toxicity Studies for *d*-Limonene

Taxonomic Group	Study Type and test material	Surrogate Species	Toxicity Values (all units in terms of measured a.i.)	MRID and Classification	Acute Toxicity Classification
Mammals	Acute Oral[a]-Technical	Mouse *(Mus musculus)*	5600 mg/kg-bw (M)	TRED, 2005	Practically Non-toxic
			6600 mg/kg-bw (F)		
		Laboratory rat (*Rattus norvegicus*)	4400 mg/kg-bw (M)		
			5100 mg/kg-bw (F)		
	Chronic[a,b]-Technical	Laboratory rat (*Rattus norvegicus*)	NOAEL: 250 mg/kg/day LOAEL: Small reductions in maternal body weight gain were observed at 500 mg/kg.[b]	RED, 1994	N/A
Birds	Acute-Oral	No Data			
	Subacute Dietary (Technical)	Bobwhite quail *(Colinus virginianus)*	LC_{50} = >5,600 mg /kg-bw No sublethal effects reported	MRID 00146988 (Acceptable)	
Terrestrial Invertebrates	Acute (contact/oral)	No Data			

Terrestrial Plants	Vegetative Vigor	Dicot-cabbage	EC_{25}: 7.09 lb a.i./A NOAEC: <7 lb a.i./A based on reductions in dry weight EC_{05} = 1.31 lb a.i./A	49098302 (Acceptable)	N/A
		Monocot-corn	EC_{25}: 2.83 lb a.i./A NOAEC: <8 lb a.i./A, based on reductions in dry weight EC_{05} =0.19 lb a.i./A		
	Seedling Emergence	Dicot	EC_{25}: Not determined NOAEC ≥265-345 lb a.i./A	49044005 (Supplemental-Qualitative)	N/A
		Monocot			

[a] Study reviewed by HED
[b] Reviewer's Note: Slight but statistically significant and dose-dependent increases in the number of liters and 10 fetuses with 14 ribs instead of 13 were observed at 500 and 1000 mg/kg/day. These effects are considered variations in skeletal formation, were not accompanied by other effects, are secondary to maternal toxicity and do not represent a concern for developmental toxicity of limonene.

V. ANALYSIS

A. Exposure Modeling

The input parameters used in this aquatic and terrestrial modeling assessment are selected from the environmental fate data available in open literature or estimated (i.e., EPI-Suite). Input parameters were generally in accordance with US EPA-OPP EFED water model parameter selection guidelines, Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides[31] or with "best professional judgment". Detailed information about the models, selection of input parameters and scenarios can be obtained from http://www.epa.gov/oppefed1/models/water/index.htm.

Aquatic Modeling

Potential aquatic exposures were initially estimated using the Surface Water Concentration Calculator (SWCC; Version 1.106, 05/22/2014) and the Pesticide Root Zone Model (PRZM, version 3.12.3, June 2006) and Exposure Analysis Modeling System (EXAMS; version 2.98.04.06, April 2005), linked with the PE5.pl input shell (November 2006). PRZM/EXAMS was used to refine the surface water exposure concentrations for aquatic exposure for the ecological assessment. Both models simulate the fate and transport of pesticides on the agricultural field (PRZM) and the fate and resulting daily concentrations of pesticides that reach an adjacent water body

[31] Parameters are selected as per Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides; Version 2.1, October 22, 2009.

through runoff, erosion, and spray drift (EXAMS). Both models consider volatilization from a surface water body, but currently only PRZM has the capacity to consider volatilization from the soil. Neither model addresses the volatilization from a plant surface (i.e., target plant). Additionally, both models were developed for "field" crops, therefore, considerable uncertainty exists when scaling down from a per acre to per square foot basis.

Simulations are based on crop-specific scenarios developed to represent environmental conditions at sites with a generally high runoff vulnerability. Aquatic ecological exposure is estimated using the "standard pond" scenario based on a 10-ha field bordering a 1-ha water body, 2-m deep (20,000 m^3) with no outlet. Weather and agricultural practices are simulated for 30 years so that the 10-year exceedance probability at the site can be estimated. The simulation was generated using 30 years of meteorological data, encompassing the years from 1961 to 1990.

Aquatic Model Inputs

The method of chemical application for both models is assumed to be ground spray (ground in SWCC) and (CAM = 1 for PRZM/EXAMS). *d*-limonene is (generally) applied as a foliar spray to weeds; both models assume the pesticide is applied to soil or foliarily to the crop by considering crop emergence and harvest dates and not the target weeds. Pesticide application management inputs and spray drift parameters are summarized in Table 8. Ground spray methods were assumed for both the preemergence and postemergence applications defined by each scenario. For the non-crop uses (i.e., spot treatment, boundary treatments, wood treatment), the application rates are assumed to be less than the crop uses (on a per acre basis).

Table 8. PRZM/EXAMS Input Parameters for *d*-Limonene

Input Parameter	Value	Reference/Discussion
#/Maximum Appl. Rate/Interval (#/lb a.i./A; reapply interval; days)	12 app @ 34.6; 2 days 6 app @ 55.2; 7 days	8.5 gallons product/A (label)
Molecular Weight (g/mole)	136.23	Calculated
Henry's Law Constant (atm-m^3/mol)	2.6 x 10^{-2}	Calculated
Vapor Pressure @ 20ºC (torr)	2	MRID 46511103
Enthalpy of Vaporization (kj/mole (kcal/mole)) REQUIRED for PRZM to include volatilization.	37.8 (9.03) to 49.9 (11.93) 10.48 = numerical mid-point between low and high values.	Chickos J.S. and Acree, W.E. 2003. http://www.chemicaldictionary.org/dic/D/D-Limonene_332.html Clara et al. 2009. J. Chem. Eng. Data 54:1087-1090.
Solubility (mg/L) @ 25ºC	13.8	Massaldi and King, 1973
Aqueous Photolysis Half-life [$t_{½}$](days)[a]	Stable	No data
Hydrolysis [$t_{½}$] @ pH 7 (days)	Stable	-
Aerobic Soil Half-life [$t_{½}$] (days)	33.53 [estimated]	Misra and Pavlostathis. 1997. Appl. Microbiol. Biotechnol. 47:572-577. Rifai and Newell, 1998. https://info.ngwa.org/GWOL/pdf/982664575.PDF

Input Parameter	Value	Reference/Discussion
		Did not multiple single value times 3[a].
Aerobic Aquatic Half-life [$t_{½}$] (days)	67.1	Estimated 2 times the aerobic soil metabolism half-life.
Anaerobic Aquatic Half-life [$t_{½}$] (days)	Stable	No data
Organic Carbon Partition Coefficient (K_{oc}) (mL/g_{oc})	1,300	Estimated range 1,030 to 4,780 CICAD#5, 1998; IPCS, 1998; 1,300 a specific value given in TOXNET, 2006
Diffusion coefficient of pesticide in air (DAIR) (cm^2/day)	4,300	PRZM Manual
Pesticide Application		
Maximum Application Rates: (EPA Reg. #; 82052-4) (EPA Reg. #; 61887-3)	Labels 12 applications @ 34.6 lb a.i/A, 2 day reapplication interval 6 applications @ 55.2 lb a.i./A, 7 day reapplication interval	
Chemical Application Method Model PRZM/EXAMS (CAM) SWCC	 Ground Spray = Soil applied CAM=1 = Ground	Defined by model
Application Efficiency (PRZM/EXAMS/SWCC)	0.99	EFED Guidance
Drop Size Distribution (PRZM/EXAMS/SWCC) *Very Fine to Fine* [EPA Reg No. 61887-3] *Fine to Medium/Coarse* [EPA Reg. No. 82052-4]	 Boom Height: Low High Low High	Ground Spray Ecological Spray Drift Fraction 0.027 0.062 0.011 0.017

[a] Although EFED guidance generally recommends multiplying single soil half-life measurements by 3 in order to account for variability, a 3x factor was not applied to the aerobic soil metabolism half-life because the biodegradability test suggested rapid degradation. Little difference was observed in the estimated EECs when the aerobic metabolism value was multiplied by 3.

Several uncertainties exist in the environmental fate input parameters in large part because many are estimates rather than measured. The aerobic soil metabolism half-life value estimated from the biodegradation rates of several monoterpenes including limonene in liquid and soil-slurry systems and the aerobic aquatic metabolism half-life was estimated from the aerobic soil metabolism value. Greater uncertainty is probably due to limitations in the volatilization routines in the models. Another major uncertainty is the use rates and number of applications of *d*-limonene.

Aquatic Modeling Results

The initial EECs (Appendix 3, Table 1) for aquatic exposure were estimated, without volatilization, for a number of uses using the SWCC. Aquatic RQs for aquatic invertebrates would exceed the LOC of 0.05 for some scenarios. The scenarios that resulted in the highest concentrations with the SWCC were rerun using PRZM/EXAMS, with PE5, with volatilization included in PRZM. The aquatic exposure EECs estimated using PRZM/EXAMS are presented in Table 9. *d*-limonene concentrations in surface water are presented for the PRZM/EXAMS with and without the volatilization routine turned on in PRZM. Volatilization reduced the peak aquatic EECs from 80 to 95% depending upon the scenario. The highest peak value across the different scenarios (323.6 μg/L) was used for the exposure value in this assessment. Representative outputs from the different models are presented in Appendix 4.

Table 9. Surface Water: Aquatic Exposure: PRZM/EXAMS *d*-limonene estimated Peak, 96-hour, 21-day and 60-day average concentrations in standard farm pond for maximum rates with and without volatilization (in PRZM).

Scenario (1st app: mn/day)	Volatilization with PRZM[b]	Peak	96-hr	21-day	60-day
		μg/L			
NC Sweet Potato (5/15)	n	2478	1737	732	340
	y	113.0	95.6	85.5	38.6
GA Pecan (5/15)	n	3542	2450	1045	464
	y	225.3	168.8	114.9	55.7
TN Nursery (3/16)	n	2179	1646	881	459
	y	217.7	177.1	116.9	57.8
NJ Nursery (01/01)	n	1659	1565	1389	784
	y	**323.6**	**309.6**	**272.0**	**210.9**
FL Strawberry (10/03)	n	2240	1625	583	244
	y	124.7	98.5	77.5	35.6

[a] Application rate: 12 application @ 34.6 lb a.i./A; 2 day interval.

[b] n is without volatilization and y is with volatilization in PRZM-(volatilization is simulated in EXAMS for both)

Terrestrial Exposure Modeling-Animals

For this assessment, the exposure scenario modeled for terrestrial animals is for a foliar spray via ground equipment, which is representative of the post- emergence/burndown herbicide uses as well as the insecticide/repellent uses (*e.g.,* ornamentals, nurseries). The EEC values used for terrestrial animal exposure are derived from the Kenaga nomograph, as modified by Fletcher *et al.* (1994), based on a large set of actual field residue data. The upper limit values from the nomograph represent high end residue values from actual field measurements (Hoerger and Kenaga, 1972). The Fletcher *et al.* (1994) modifications to the Kenaga nomograph are based on measured field residues from 249 published research papers, including information on 118 species of plants, 121 pesticides, and 17 chemical classes.

Terrestrial exposure estimates (EECs) for avian and mammalian risk assessments were derived using the T-REX model (version 1.5.1) (Tables 10-14) and were based on the products with the highest application rates for the different use patterns (Table 2). The default 35-day foliar half-life value was used for modeling EECs on terrestrial food items, however, see the Risk Description section for further discussion regarding a shorter half-life value. A complete description of the input parameters and output is contained in APPENDIX 5.

Table 10. EECs on Potential Food Items Following Label-Specified Applications of *d*-limonene Using the T-REX Model (ppm).

USE	Rate (lb a.i./A)	DIETARY-BASED EECs	KENAGA VALUES (Upper Bound)
Orange Guard- Ornamental *6 apps. ; 7-day retreatment interval*	4.6	Short Grass	4,816
		Tall Grass	2,207
		Broadleaf plants	2,709
		Fruits/pods/seeds	301
		Arthropods	1,886
	18.4	Short Grass	19,265
		Tall Grass	8,830
		Broadleaf plants	10,836
		Fruits/pods/seeds	1,204
		Arthropods	7,545
	55.2	Short Grass	57,795
		Tall Grass	26,489
		Broadleaf plants	32,509
		Fruits/pods/seeds	3,612
		Arthropods	22,636
Avenger Burndown Herbicide Agricultural Crops *12 apps.; 2-day retreatment interval*	*34.6*	Short Grass	80,893
		Tall Grass	37,076
		Broadleaf plants	45,502
		Fruits/pods/seeds	5,056
		Arthropods	31,683

Table 11. Avian Dose-based EECs (mg/kg-bw)/Avian Classes and Body Weights (grams) for Orange Guard- Ornamental plants in Greenhouses, nurseries, Christmas tree plantations, and landscapes (6 applications per year, 7-day retreatment interval)

	Rate= 4.6 (lb a.i./A)			Rate=18. 4 (lb a.i./A)			Rate= 55.2 (lb a.i./A)		
Food Item	Small	Med.	Large	Small	Med.	Large	Small	Med.	Large
Short Grass	5,485	3,128	1,400	21,941	12,512	5,602	65,822	37,535	16,805
Tall Grass	2,514	1,434	642	10,056	5,734	2,567	30,169	17,203	7,702
Broadleaf plants	3,085	1,759	788	12,342	7,038	3,151	37,025	21,113	9,453
Fruits/pods	343	195	88	1,371	782	350	4,114	2,346	1,050
Arthropods	2,148	1,225	548	8,593	4,900	2,194	25,780	14,701	6,582
Seeds	76	43	19	305	174	78	914	521	233

Table 12. Avian Dose-based EECs (mg/kg-bw)/Avian Classes and Body Weights (grams)-Avenger Burndown Herbicide – Agricultural Crops (12 applications per year, 2-day retreatment interval)

Food Item	Rate-34.6 lb a.i./A		
	small	med.	large
Short Grass	92,129	52,536	23,521
Tall Grass	42,226	24,079	10,780
Broadleaf plants	51,823	29,551	13,231
Fruits/pods	5,758	3,283	1,470
Arthropods	36,084	20,577	9,212
Seeds	1,280	730	327

Table 13. Mammalian Dose-based EECs (mg/kg-bw)/Mammal Size Classes and Body Weights (grams) for Orange Guard- Ornamental plants in greenhouses, nurseries, Christmas tree plantations, and landscapes (6 applications per year, 7-day retreatment interval)

Food Item	Rate= 4.6 (lb a.i./A)			Rate= 18.4 (lb a.i./A)			Rate= 55.2 (lb a.i./A)		
	Small	Med.	Large	Small	Med.	Large	Small	Med.	Large
Short Grass	4,592	3,174	736	18,368	12,694	2,943	55,103	38,083	8,830
Tall Grass	2,105	1,455	337	8,418	5,818	1,349	25,255	17,455	4,047
Broadleaf plants	2,583	1,785	414	10,332	7,141	1,656	30,995	21,422	4,967
Fruits/pods	287	198	46	1,148	793	184	3,444	2,380	552
Arthropods	1,798	1,243	288	7,194	4,972	1,153	21,582	14,916	3,458
Seeds	64	44	10	255	176	41	765	529	123

Table 14. Mammalian Dose-based EECs (mg/kg-bw)/Mammal Size Classes and Body Weights (grams) for Avenger Burndown Herbicide – Agricultural Crops (12 applications per year, 2-day retreatment interval)

Food Item	Rate-34.6 lb a.i./A		
	small	med.	large
Short Grass	77,125	53,304	12,359
Tall Grass	35,349	24,431	5,664
Broadleaf plants	43,383	29,983	6,952
Fruits/pods	4,820	3,331	772
Arthropods	30,207	20,877	4,840
Seeds	1,071	740	172

Plants

Exposure to terrestrial plants is estimated using the TerrPlant (v1.2.2) screening model. TerrPlant estimates potential exposure from a single application using default assumptions for runoff (2% given solubility is between 10 and 100 ppm) and spray drift (1% given a ground application of a liquid formulation) (Table 15). Because there were no effects in the seedling emergence study, this assessment only considers the exposure via spray drift (runoff is not included). See APPENDIX 6 for more information.

Table 15. EECs on Plants Following Label-Specified Ground Applications of *d*-limonene Using the TerrPlant Model (lb a.i./A)

USE	RATE (lb a.i./A)	EECs from Spray Drift
Orange Guard- Ornamental	18.4	0.184
	55.2	0.551
Avenger Burndown-Ag. Crops	34.6	0.346

VI. Risk Characterization

A. Risk Estimation - Integration of Exposure and Effects Data

Toxicity data and exposure estimates are used to evaluate the potential for adverse ecological effects on non-target species. For this screening-level assessment of *d*-limonene the deterministic risk quotient method is used to provide a metric of potential risks. The RQ is a comparison of exposure estimates to toxicity endpoints; estimated exposure concentrations are divided by acute and chronic toxicity values. The resulting unitless RQs are compared to the Agency's levels of concern (LOCs) (see Table 16), which are the Agency's interpretive policy such that when LOCs are exceeded, the need for regulatory action may be considered. These criteria are used to indicate when the use of a pesticide, as directed on the label, has the potential to cause adverse effects on non-target organisms.

Table 16. Agency Levels of Concern (LOC).

Risk	Description	RQ	Taxa
Acute	Potential for acute risk to non-target organisms which may warrant regulatory action in addition to restricted use classification	acute RQ > 0.5	aquatic animals, mammals, birds
Acute Listed Species	Listed species may be potentially affected by use	acute RQ > 0.05	aquatic animals
		acute RQ > 0.1	mammals and birds
Chronic	Potential for chronic risk may warrant regulatory action, listed species may potentially be affected through chronic exposure	chronic RQ > 1	all animals
Non-Listed and Listed Plant	Potential for effects in non-listed and listed plants	RQ > 1	all plants

1. Non-target Aquatic Animals and Plants

On an acute exposure basis, *d*-limonene is classified as "slightly toxic" to freshwater fish and invertebrates. With a peak EEC of 323.6 ug a.i./L, the resulting RQ values were below the LOC thresholds (acute and ES) at 0.004 and 0.0083 for fish and invertebrates, respectively (Table 17). However, this is based on a limited toxicity set with only one species of freshwater fish tested and no data for estuarine/marine (E/M) species (fish or invertebrates). In the absence of data, the freshwater species will serve as a surrogate for E/M species, however, there is uncertainty with using freshwater values as a proxy for E/M species, especially given that only one species of freshwater fish was tested.

Toxicity data are not available to assess the risk to fish and invertebrates on a chronic exposure basis. Based on the highest 60-day EEC (210.9 ug/L), and the acute toxicity value for fish (80,000 ug/L), *d*-limonene would need to be 379 times more toxic on a chronic exposure basis to reach the level of concern. Likewise, for invertebrates, based on the highest 21-day EEC (272 ug/L) and the acute toxicity value (39,000 ug/L), *d*-limonene would need to be 143 times more toxic on a chronic exposure basis to reach the level of concern. In an attempt to gain further information on the chronic risk, a structure activity analysis (QSAR) was run but it did not provide useful information because of the poor fit with the available acute data. When chronic data are lacking, an acute to chronic ratio (ACR) may be used to inform for the taxa, but with no chronic data for *d*-limonene, this type of analysis is not possible for the active ingredient. As an alternative, Raimondo et. al, (2007)[32] provides an ACR value based on a dataset of 456 same species pairs of acute and chronic data. Using the 90^{th} percentile ACR values of 90.0 and 68.3 for fish and invertebrates, respectively, there would not be any exceedances at the highest application rate. There is, however, a high degree of variability in the estimated ACRs with ranges of (1.2-2,121) for fish and (1.1-18,550) for invertebrates. While the majority of chemicals will likely have ACRs at or below the 90^{th} percentile mentioned above, there is the uncertainty of over or underestimating the chronic risk given the high variability in the dataset. Based on the 90^{th} percentile ACR, risk is not anticipated at this time.

There are no LOC exceedances for vascular and non-vascular aquatic plants.

Table 17. Aquatic Exposure RQ Values for *d*-Limonene

Taxonomic Group	Exposure Type	Toxicity (ug/L)	EEC (µg/L)	RQ	Exceeds LOC (Y/N)
Freshwater Fish	Acute	LC_{50} = 80,000	323.6	0.004	N
Freshwater Invertebrate	Acute	LC_{50} = 39,000	323.6	0.008	N
	Non-listed	EC_{50} = 9,353	323.6	0.035	N

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[32] Raimondo, S, Montague, B. , and Barron, M. (2007) Determinants of Variability in Acute to Chronic Ratios for Aquatic Invertebrates and Fish. *Environ Toxicol Chem* (26) No. 9 pp 2019-2023.

Taxonomic Group	Exposure Type	Toxicity (ug/L)	EEC (µg/L)	RQ	Exceeds LOC (Y/N)
Aquatic Vascular plants	Listed	NOAEC =1,731	323.6	0.187	N
Aquatic Non-Vascular	Non-listed	EC_{50} =29,650	323.6	0.011	N
	Listed	NOAEC = 3,125	323.6	0.104	N

Non-Target Terrestrial Animals

Mammals

For the Orange Guard uses at the higher application rates (i.e., 18.4 and 55.2 lb a.i./A), there were acute and endangered species (ES) LOC exceedances for the majority of size/dietary class combinations (Table 18). The shaded cells indicate the acute LOC (0.5) exceedances and the bold indicate the additional ES LOC (0.1) exceedances. The acute exceedances (i.e., LOC ≥0.5) range from 0.64-1.9 for the 18.4 lb a.i. rate and from 1.02-5.7 for the 55.2 pounds a.i./A rate.

In terms of chronic exposure, there were LOC exceedances (i.e., LOC ≥ 1.0) for the majority of size/dietary class combinations and the exceedances ranged from 0.96-33 and 1.19-100 for the 18.4 and 55.2 lb a.i./A rates, respectively.

For the lower rate (4.6 lb a.i./A), the acute RQ was exceeded for the small mammal eating short grass exclusively (RQ=0.47) and the ES LOC was exceeded for all size classes eating short grass, tall grass, and broadleaf plants and the small and medium mammals consuming arthropods (Table 18).

On a chronic exposure basis, there were exceedances that ranged from 1.5-8.4 for the 4.6 pounds a.i./A rate.

For the Avenger Burndown uses at the 34.6 lb a.i./A, applied every 2 days for a total of 12 applications, the RQs are higher than the scenarios for the Orange Guard. The acute RQs exceedances ranged from 0.5-7.98 and the chronic exceedances ranged from 1.67-140 (Table 19).

Table 18. Mammalian Dose Based RQs - Orange Guard Ornamental plants in Greenhouses, nurseries, Christmas Tree plantations, and landscapes (6 applications per year, 7-day retreatment interval)

Food Item	Rate 4.6 lb a.i./ A					
	Small=15 g		Medium=35g		Large-1000g	
	Acute	Chronic	Acute	Chronic	Acute	Chronic
Short Grass	0.47	8.36	0.41	7.14	0.22	3.83
Tall Grass	0.22	3.83	0.19	3.27	0.10	1.75
Broadleaf plants	0.27	4.70	0.23	4.02	0.12	2.15
Fruits/pods	0.03	0.52	0.03	0.45	0.01	0.24
Arthropods	0.19	3.27	0.16	2.80	0.09	1.50
Seeds	0.01	0.12	0.01	0.10	0.00	0.05
	Rate 18.4 lb a.i./ A					
Short Grass	1.90	33.43	1.62	28.55	0.87	15.31
Tall Grass	0.87	15.32	0.74	13.09	0.40	7.02
Broadleaf plants	1.07	18.80	0.91	16.06	0.49	8.61
Fruits/pods	0.12	2.09	0.10	1.78	0.05	0.96
Arthropods	0.74	13.09	0.64	11.18	0.34	5.99
Seeds	0.03	0.46	0.02	0.40	0.01	0.21
	Rate 55.2 lb a.i./ A					
Short Grass	5.70	100.29	4.87	85.66	2.61	45.92
Tall Grass	2.61	45.96	2.23	39.26	1.20	21.05
Broadleaf plants	3.21	56.41	2.74	48.19	1.47	25.83
Fruits/pods	0.36	6.27	0.30	5.35	0.16	2.87
Arthropods	2.23	39.28	1.91	33.55	1.02	17.98
Seeds	0.08	1.39	0.07	1.19	0.04	0.64

Table 19. Mammalian Dose Based RQs - Avenger Burndown Herbicide – Agricultural Crops (12 applications per year, 2-day retreatment interval)

Dose-based RQs (Dose-based EEC/LD50 or NOAEL)	Rate 34.6 lb a.i./ A					
	Small=15 g		Medium=35g		Large-1000g	
	Acute	Chronic	Acute	Chronic	Acute	Chronic
Short Grass	7.98	140.37	6.81	119.90	3.65	64.27
Tall Grass	3.66	64.33	3.12	54.95	1.67	29.46
Broadleaf plants	4.49	78.96	3.83	67.44	2.05	36.15
Fruits/pods	0.50	8.77	0.43	7.49	0.23	4.02
Arthropods	3.12	54.98	2.67	46.96	1.43	25.17
Seeds	0.11	1.95	0.09	1.67	0.05	0.89

Birds

The toxicity data set for birds is limited as there are no acute oral or reproductive studies (chronic exposure). Based on the available dietary exposure study, *d*-limonene is classified as "practically non-toxic" with an LC_{50} value of >5,600 mg a.i./kg diet. Since the endpoint from this study is non-definitive (*i.e.,* it is a 'greater than' value), it will not be used to calculate RQs.

Terrestrial Invertebrates

Data are not available to assess the risk to invertebrates.

Non-target Terrestrial Plants

The risk to plants was assessed using TerrPlant (**Appendix 6**) and then refined with an analysis using AgDrift (**Appendix 7**). From the TerrPlant analysis, there were no RQ exceedances for applications at the 4.6 or 18.4 lb a.i./A rate. At the 34.6 and 55.1 lb a.i./A rates, there were LOC exceedances (RQs= 1.8 and 2.9, respectively) for listed monocots (**Table 20**).

Table 20. Screening Level Analysis-Terr Plant RQs

	Rate lb a.i./A		
Plant Type	18.4	34.6	55.1
Monocot	<0.1	0.12	0.20
Monocot (listed)	0.97	**1.82**	**2.91**
Dicot	<0.1	<0.1	<0.1
Dicot (listed)	0.14	0.26	0.42

Using the Ag Drift analysis, at the 4.6 lb a.i./A rate, the distance to no longer exceed the LOC was 0-3 feet for non-listed species and 3-23 feet for listed species. For the higher rates (18.4-55.1 lb a.i./A, the distance ranged from 3-19 feet for non-listed species and 9-305 feet for listed species **(Table 21**).

Table 21. Ag Drift Analysis-Distance from the Field to no longer exceed the LOC

Product	Rate	Plant Type	Listed	Non-listed
Avenger Med-Coarse Droplet	34.6	Monocot	75.46	6.56
		Dicot	9.84	3.23
Orange Guard (Fine Droplet)	4.6	Monocot	22.97	3.28
		Dicot	3.28	0
	18.4	Monocot	91.86	6.56
		Dicot	13.2	3.28
	55.2	Monocot	305.11	19.68
		Dicot	39.37	9.84

B. Risk Description

Risks to Aquatic Organisms

Animals
On an acute exposure basis, the risk to freshwater fish and invertebrates is considered low. Data are not available for estuarine/marine (E/M) species (fish or invertebrates). In the absence of data, the freshwater species may serve as a surrogate for E/M species, thus, the acute risk is anticipated to be low. However, there is uncertainty given the paucity of data for *d*-limonene.

Toxicity data are not available to assess the risk to fish and invertebrates on a chronic exposure basis. Using the 90^{th} percentile ACR (see earlier discussion of Raimondo et. al., in Risk Characterization) to estimate the chronic toxicity values, risk is not anticipated for fish or invertebrates at this time. However, given the high variability in the ACR analysis, having chronic data for *d*-limonene would greatly reduce the uncertainty in this assessment.

Plants
All of the RQs for aquatic vascular and non-vascular plants are below the LOCs for risk to listed and nonlisted species. Therefore, likelihood of direct risk to aquatic plants from the use of *d*-limonene is considered low.

Risks to Terrestrial Organisms

Mammals
d-limonene is classified as "practically non-toxic" to mammals on an acute oral basis, however, because of the high application rates and frequency of applications, the expected residues on the dietary items are high at the 18.4, 34.6 and 55.1 lb a.i./A application rates/use scenarios, thus leading to exceedances for the majority of size/dietary class combinations. At the 4.6 lb a.i./A rate, the only exceedance for was the small mammal feeding exclusively on short grass.

There is uncertainty with the exposure to terrestrial organisms for several reasons. Based on the chemical properties/environmental fate data, *d*-limonene is expected to volatilize rapidly (with a vapor pressure of <3 mm of Hg). At this time there is only one study (MRID 47548301) that characterizes the foliar dissipation half-life and a minimum of 3 studies are needed to move away from the 35-day default assumption in the TREX model. To further explore the risk to terrestrial animals from exposure to *d*-limonene, the available magnitude of residues study was reviewed and is considered here. The magnitude of residue study for mustard greens (MRID 47548301) tested two products (QRD 400/QRD 416 which contained a mixture of 3 active ingredient terpenes, *α*-terpinene, *ρ*-cymene, and *d*-limonene) that were applied to mustard green foliage at a rate of 2.6 and 2.4 lb a.i./A for QRD 400 and QRD 416, respectively. Leaves were harvested at 0-, 1-, and 4- hours. *d*-limonene levels generally dropped below the Limit of Quantification (LOQ=0.05 ppm) at 1-hour. The rate of decline for *d*-limonene ranged from 2.8 to 4.67^{-hr}. Adjusting the 2.4 or 2.6 lb a.i./A to the maximum rate for d-limonene (34.6 lb a.i./A), the time required for the *d*-limonene concentrations to drop below the LOQ ranged between 3 and

15 hours. This shorter half-life also seems in-line with the registrant suggested reapplication intervals as short as every 2 days. To explore the expected residues on food items, the T-REX model was run using a foliar dissipation half-life of 2 days. When the high end exposure scenario (34 lb a.i./A, 12X, 2-day interval) was modeled, the acute RQ exceedances ranged from 0.5- 1.6 and the chronic RQs ranged from 1.5- 28 for a variety of size/dietary classes. The lower exposure scenario (4.6 lb a.i./A, 6X, 7-day interval), did not have any acute LOC exceedances (the ES LOC of 0.1 was exceeded to small mammals feeding on short grass; RQ = 0.12) and for chronic exposure, there were exceedances for small and medium mammals feeding on short grass and broadleaf plants with RQs around 1.01-2.10.

Based on the available data, there are risks (acute and chronic) identified for mammals at the higher foliar exposure scenarios (18.4, 34.6 and 55.1 lb a.i./A rates). At the lower rate of 4.6 lb a.i./A (using the 2-day half-life), risk to mammals (acute) is not anticipated. While there is an endangered species LOC exceedance (RQ=0.12) it is only for the 15 gram mammal feeding exclusively on short grass. To refine further, the LD_{50} was reported separately for males and females and the lowest value [4400 mg a.i./kg-bw (M)] was used for the endpoint in this risk assessment but if the higher value [5100 mg a.i./kg-bw (F)] was used then there would be no exceedances, thus, the risk is between an RQ of 0.10 and 0.12 for the 4.6 lb a,i./A rate.

On a chronic exposure basis, there were exceedances for small and medium mammals feeding on short grass and broadleaf plants with RQs around 1.01-2.10. The TREX model indicates that these exceedances would occur in 17 out of the 56 days (the application pattern is 6 applications every 7 days), thus, the exceedances are likely occurring the day of application and lasting 1-2 days. For additional characterization, because the effect was a small reduction in maternal weight gain, the LOAEC value (500 mg a.i./kg-bw) was used to gauge if exceedances would occur at the actual dose that caused the effect. When modeling the endpoint of 500 mg a.i./kg-bw, the only chronic exceedance was an RQ of 1.05 for the 15 gram mammal feeding exclusively on short grass. Altogether, the risk to mammals is not considered high at the lowest application scenario. Additional data for the foliar dissipation half-life would reduce the uncertainty in this analysis.

Birds

Because there was no mortality or sublethal effects at the highest treatment level tested for birds (dietary study only), the RQs for acute or chronic effects to birds were not calculated in the Risk Estimation section of this assessment. Therefore, in order to gain a better understanding of how the EECs for the application rates for *d*-limonene relate to the toxicity data currently available, a ratio of the EEC/acute endpoint was calculated under the assumption that the highest level tested is the endpoint value. While this analysis is of limited utility for the high rates (18.4, 34.6, 55.1 lb a.i./A) because the highest treatment level the animal was exposed to was lower than the EECs by a large margin for the majority of feed items, it can provide useful information for the lower rate. At 4.6 lb a.i./A., the EEC of 4816 ppm is lower than the highest test concentration (5600 ppm) at which no mortality or sublethal effects were observed, thus, the risk to birds on an acute exposure basis is considered to be low.

As discussed in the mammal section above, there is uncertainty with regard to the foliar dissipation half-life. In order to explore the shorter half-life of 2-days, the EECs from TREX with a 2-day foliar dissipation half-life were compared to the 5600 ppm endpoint. The risk to birds at the lowest rate was low. In contrast to using the default half-life, when using the shorter half-life, the 18.4 lb a.i./A rate could also be analyzed because the EECs were below the highest test concentration in the toxicity test. For the 18.4 lb a.i./A application scenario, the EEC of 4844 ppm is lower than the highest test concentration at which no mortality or sublethal effects were observed (5600 ppm), thus, the risk to birds on an acute exposure basis is considered to be low.

Based on the available data, risk is presumed for the highest application scenarios (the 34.6 and 55.1 lb a.i./A rates). While there is uncertainty because the only data available is from a dietary study (which may underestimate the risk compared to an acute oral study), and a sufficient number of foliar dissipation values are not available at this time, the risk to birds from the lower rates of 4.6 and 18.4 lb a.i./A is considered to be low. An acute oral study (tested up to environmentally relevant EECs or within the physiological limits of the bird) and additional data for the foliar dissipation half-life would reduce the uncertainty in this analysis. Additionally, the risk for birds on a chronic exposure basis is uncertain without data.

Terrestrial invertebrates

Due to a lack of toxicity data, at this time the risk to terrestrial invertebrates is presumed given that *d*-limonine is registered as an insecticide.

Terrestrial Plants

Two different analyses were used to assess the risk to terrestrial plants. In the screening level analysis with TerrPlant, there were no RQ exceedances for applications at the 4.6 or 18.4 lb a.i./A rate. At the 34.6 and 55.1 lb a.i./A rates, there were LOC exceedances (RQs= 1.8 and 2.9, respectively) for listed monocots.

Using the Ag Drift analysis, different factors related to the droplet size were incorporated based on language for reducing spray drift on the Avenger label. For this assessment, the Avenger use (34.6 lb a.i./A) was assigned to a medium-coarse droplet and the other assessed rates (Orange Guard label) were assigned to the default-fine droplet size. At the 4.6 lb a.i./A rate, the distance to no longer exceed the LOC was 0-3 feet for non-listed species and 3-23 feet for listed species. For the higher rates (18.4-55.1 lb a.i./A), the distance ranged from 3-19 feet for non-listed species and 9-305 feet for listed species.

Based on these analyses, there is a risk identified from spray drift to non-target listed and non-listed plants with the exception of non-listed dicots at the 4.6 lb a.i./A rate. There was one “minor” plant damage incident reported as well (See Review of Incident data).

Review of Incident Data

Reviews of the Ecological Incident Information System (EIIS) and the Avian Incident Monitoring System (AIMS)[33] were conducted on 9/18/14. There are no reported incidents for *d*-limonene in the EIIS or AIMS databases. In addition to the incidents recorded in EIIS and AIMS, additional pesticide incidents are reported to the Agency in aggregated incident reports. Ecological incidents reported in aggregate reports include those categorized as 'minor fish and wildlife' (W-B), 'minor plant' (P-B), and 'other non-target' (ONT) incidents. 'Other non-target' incidents include reports of adverse effects to insects and other terrestrial invertebrates. A query of the aggregate incident report on 9/25/14, found a single incident reported for HOME DEFENSE INDOOR INSECT KILLER-RTU (EPA product number: 045987-000239). The incident was reported as 'minor plant' damage during the time period of 4/1/04 -6/30/04. No further information is available.

Federally Threatened and Endangered (Listed) Species Concerns

Before completing this Registration Review, the Agency will conduct an ecological risk assessment to address the Agency's obligations under both the Endangered Species Act (ESA) and FIFRA. While the risk assessment supporting this proposed interim Registration Review decision evaluates risks to species that are not subject to the ESA, EPA is still in the process of conducting a risk assessment for endangered and threatened (listed) species and their designated critical habitats for *d*-limonene. In this proposed interim decision, therefore, EPA has not completed effects determinations for listed species associated with the registered uses of *d*-limonene.

At this time, EPA has not fully developed its risk assessment process for listed species. In November 2013, the EPA, along with the U.S. Fish & Wildlife Service (USFWS), the National Marine Fisheries Service (NMFS) (collectively, the Services), and the U.S. Department of Agriculture (USDA) released a summary of their joint Interim Approaches for assessing risks to listed species from pesticides. The Interim Approaches were developed jointly by the Agencies in response to the National Academy of Sciences' (NAS) recommendations and reflect a common approach to risk assessment shared by the Agencies as a way of addressing scientific differences between the EPA and the Services. The NAS report, available at http://www.nap.edu/catalog.php?record_id=18344, outlines recommendations on specific scientific and technical issues related to the development of pesticide risk assessments that EPA and the Services must conduct in connection with their obligations under the ESA and FIFRA. The joint Interim Approaches were released prior to a stakeholder workshop held on November 15, 2013. In addition, the EPA presented the joint Interim Approaches at the December 2013 Pesticide Program Dialogue Committee (PPDC) and State-FIFRA Issues Research and Evaluation Group (SFIREG) meetings, allowing additional opportunities for stakeholders to comment on the Interim Approaches. As part of a phased, iterative process for developing the Interim Approaches, the Agencies will also consider public comments on the Interim Approaches in connection with the development of upcoming Registration Review decisions. The details of the

[33] http://www.abcbirds.org/abcprograms/policy/pesticides/aims/aims/index.cfm

joint Interim Approaches are contained in the white paper "Interim Approaches for National-Level Pesticide Endangered Species Act Assessments Based on the Recommendations of the National Academy of Sciences April 2013 Report," dated November 1, 2013, available at http://www.epa.gov/espp/2013/nas.html.

Clean Water Act

Limonene is not identified as a cause of impairment for any water bodies listed as impaired under section 303(d) of the Clean Water Act, based on information provided at http://iaspub.epa.gov/tmdl_waters10/attains_nation_cy.cause_detail_303d?p_cause_group_id=885. In addition, no Total Maximum Daily Loads (TMDL) have been developed for limonene, based on information provided at http://iaspub.epa.gov/tmdl_waters10/attains_nation.tmdl_pollutant_detail?p_pollutant_group_id=885&p_pollutant_group_name=PESTICIDES. More information on impaired water bodies and TMDLs can be found at http://www.epa.gov/owow/tmdl/.

Endocrine Disruptor Screening Program

As required by FIFRA and FFDCA, EPA reviews numerous studies to assess potential adverse outcomes from exposure to chemicals. Collectively, these studies include acute, subchronic and chronic toxicity, including assessments of carcinogenicity, neurotoxicity, developmental, reproductive, and general or systemic toxicity. These studies include endpoints which may be susceptible to endocrine influence, including effects on endocrine target organ histopathology, organ weights, estrus cyclicity, sexual maturation, fertility, pregnancy rates, reproductive loss, and sex ratios in offspring. For ecological hazard assessments, EPA evaluates acute tests and chronic studies that assess growth, developmental and reproductive effects in different taxonomic groups. As part of its reregistration decision for *d*-limonene, EPA reviewed these data and selected the most sensitive endpoints for relevant risk assessment scenarios from the existing hazard database. However, as required by FFDCA section 408(p), *d*-limonene is subject to the endocrine screening part of the Endocrine Disruptor Screening Program (EDSP).

EPA has developed the EDSP to determine whether certain substances (including pesticide active and other ingredients) may have an effect in humans or wildlife similar to an effect produced by a "naturally occurring estrogen, or other such endocrine effects as the Administrator may designate." The EDSP employs a two-tiered approach to making the statutorily required determinations. Tier 1 consists of a battery of 11 screening assays to identify the potential of a chemical substance to interact with the estrogen, androgen, or thyroid (E, A, or T) hormonal systems. Chemicals that go through Tier 1 screening and are found to have the potential to interact with E, A, or T hormonal systems will proceed to the next stage of the EDSP where EPA will determine which, if any, of the Tier 2 tests are necessary based on the available data. Tier 2 testing is designed to identify any adverse endocrine-related effects caused by the substance, and establish a dose-response relationship between the dose and the E, A, or T effect.

Under FFDCA section 408(p), the Agency must screen all pesticide chemicals. Between October 2009 and February 2010, EPA issued test orders/data call-ins for the first group of 67 chemicals, which contains 58 pesticide active ingredients and 9 inert ingredients. A second list of chemicals identified for EDSP screening was published on June 14, 2013[34] and includes some pesticides scheduled for registration review and chemicals found in water. Neither of these lists should be construed as a list of known or likely endocrine disruptors.

For further information on the status of the EDSP, the policies and procedures, the lists of chemicals, future lists, the test guidelines and the Tier 1 screening battery, please visit our website.[35]

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[34] See http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPPT-2009-0477-0074 for the final second list of chemicals.

[35] http://www.epa.gov/endo/

Appendix 1. Summary of Labeled Uses for d-Limonene

Crops or Use Site	%AI	Formulation/ Equipment	Max App Rate (lb a.i./A; unless noted)	Maximum # of Appl. per Season/Inter-val (days)	Maximum lb a.i./A/Season (year)	Comments
Commercial/Inst./ Household/ dwelling; Spot treatment, crack & crevice, surface spray, direct spray	10	Aerosol can	NS	As needed	NS	Spray for 10 sec.
Commercial/Inst./ Household Crack & crevice Outdoor general spray Surface treatment	4.0	Aerosol can	0.031 lb a.i./200 ft^2	NS	NS	15 oz container/ 200 ft^2 0.031 lb a.i./200 ft^2
RTU-Pet Shampoo	5	Liquid	0.429 lb a.i./gal 0.04 lb a.i./12 oz	NS /7	NS	
Sponge on, dip, sprinkle	78	EC	NS	NS	NS	1.5 oz/1 gal (product) 0.663 lb a.i./bead
Residential/turf Outdoor general surface spray, lawns Crack & crevice spray	1	Aerosol/RTU-Spray	NS	Do not apply more than 1 time per day/	NS	Aerosol can, 0.0826 lb a.i./gal RTU-0.009 lb a.i./14floz
Household/ dwellings Crack & crevice treatment ; indoor and outdoor general surface spray; perimeter treatment	5.8	RTU-Sprayer	NS Saturate area	NS	NS	8.139 lb/gal 0.47 lb a.i./gal
Household/ Commercial/ Institutional Fire ant mound crack & crevice spray; directed spray, mound drench; perimeter treatment	5.8	Sprayer	0.2265 lb a.i./mound	NS	NS	1 to 3 (4) Sprayer ; 0.5 gal/mound Spray volume per Area not specified. Assuming 40 mounds per A= 9.06 lb a.i./A

Crops or Use Site	%AI	Formulation/ Equipment	Max App Rate (lb a.i./A; unless noted)	Maximum # of Appl. per Season/Inter-val (days)	Maximum lb a.i./A/Season (year)	Comments
Ornamental plants in greenhouses, nurseries, Christmas tree plantations, and landscapes (residential commercial, industrial)	5.8	Pump sprayer Handheld sprayer Ground	4.6	6/7	27.6	Rates were expressed as dilution of (1:4; 0.092 lb a.i./gal water), or (1:6) with various finish spray volumes. “row crops 25-50 gal/A; vine crops 50-200 gal/A, tree crops 100-400 gal/A, greenhouse 100 gal /10,000 sq ft, 600 gal per A-forestry”.
			18.4	6/7	110.4	
			36.8	6/7	220.8	
			40.1	6/7	240.6	
			55.2	6/7	331.2	
Void treatment; wood surface treatment;	95	RTU Injection eq.	5.19 lb a.i./100 ft^2	As needed	NS	1 oz/ft^2 0.052 lb a.i./ft^2
Soil drench/ Soil treatment (fire ant)	78.2	Pump spray bottle	0.3534 lb/2 gal; 0.0883 lb/0.5 gal	NS	NS	
Household/outdoor premises Crack & crevice	10	RTU Aerosol can	NS	NS	NS	Aerosol can; Spray for 10 seconds
Commercial/premises Cracks & crevice; general surface	4.0	RTU Sprayer	0.030 lb a.i./200 ft^2	As needed	NS	0.246 lb a.i./gal-27 gal/A
Treated strip; clothing treatment; skin contact	4.0	Wrist band/ Impreg. material	NS	As needed	NS	
Borders around driveways, patios, sidewalks, mature trees and ornamentals, buildings, residential greenhouses, fencerows, flowerbeds	Conc. (70%)/ RTU (17.5 %)	Sprayer	1.28-1.47 lb a.i./gal (dilution) 51-59 lb a.i./A*	12 Weed post-emergence	NS	*Assumed 40 gallons per A because the label did not have a finish spray volume to complete the rate. Need further clarification on label to reduce uncertainty. Given the uncertainty and the use as perimeter/spot treatment, this assessment will use the high scenarios above to inform on the risk for this use.

Crops or Use Site	%AI	Formulation/ Equipment	Max App Rate (lb a.i./A; unless noted)	Maximum # of Appl. per Season/Inter-val (days)	Maximum lb a.i./A/Season (year)	Comments
Ag. Crops: Brassica veg; citrus; grapes; herbs; leafy veg; legume veg; pome fruit; root & tuber Weed post-emergence/ burndown	55%	Ground Sprayer-Directed/ Hooded sprayer Broadcast and Spot treatment	34.6	12 (2)	NS	Label states do not exceed 8.5 gallons of product per acre per application (4.07 lb a.i./gal * 8.5 gal/A= 34.60 lb a.i./A).
Household/domestic dwellings outdoor premises; residential lawns.	23	RTU Garden hose-end sprayer	0.454 lb a.i/1000 ft^2 (19.79)	12	NS	For control of algae and moss.

Appendix 2. Estimation Aerobic Metabolism

Misra and Pavlostathis[36] (1997) conducted batch experiments to evaluate biodegradation rates of several monoterpenes, including limonene, in liquid and soil-slurry systems, under aerobic conditions. Biodegradations was demonstrated through the depletion of the monoterpene mass, CO_2 production, and a corresponding increase in biomass. In liquid cultures with no soil, monoterpene degradation followed a Monod or Michaelis-Menten type kinetics equation (Rafai and Newell, 1998)[37] (eq. 1),

$$\mu = -\mu_{max} * \frac{S}{Ks+S} \qquad \text{(eq. 1)}$$

where µ is the specific growth rate, s (mg/L) is the concentration in solution, t is time (days), μ_{max} is the maximum reaction rate (mg/L per day), and K_s (mg/L) is the substrate saturation constant (i.e., saturation constant at half μ_{max}). In the Monod model, the growth rate is related to the concentration of a growth limiting substrate through the parameters μ_{max} and K_s (Rifai and Newell, 1998; Okpokwasili and Nweke[38], 2005). Additionally, Monod related the yield coefficient ($Y_{x/s}$) eq. 2 to the specific rate of biomass growth (µ) and the specific rate of substrate utilization (q) (eq. 3).

$$Y_{x/s} = \frac{dx}{ds} \qquad \text{(eq. 2)}$$

$$\mu = Y_{x/s}/X \;.\; \frac{ds}{dt} \approx Y_{x/s*q} \qquad \text{(eq. 3)}$$

Further, Rifai and Newell (1998) provided a method to estimate a first-order decay rate to estimate a half-life for input into the fate models. They suggest that high values of K_s (i.e., $K_s >> S$) the Monod equation simplifies to eq. 4.

$$\frac{dS}{dt} = -u_{max} \frac{S}{Ks} \qquad \text{(eq. 4)}$$

And that the first-order decay constant, k, (day^{-1}) is estimated from the expression μ_{max}/K_s.

Misra and Pavlostathis (1997) reported in values (Table 2) for $-\mu_{max}$ 0.022 and 0.024 (h^{-1}) and K_s 17 and 32 (mg l^{-1}) for solutions below and above solubility, respectively. These values result in half-life estimates of 22.7 and 38.5 days for below and above solubility, respectively.

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[36] Misra and Pavlostathis. 1997. Appl. Microbiol. Biotechnol. 47:572-577.
[37] Rifai and Newell, 1998. https://info.ngwa.org/GWOL/pdf/982664575.PDF
[38] Okpokwasili, G.C. and C.O. Nweke, 2005. Microbial growth and substrate utilization kinetics. African J. Biotech. 5:305-317.

Appendix 3. SWCC EEC

Table 1. SWCC *d*-limonene estimated Peak, 96-hour, 21-day and 60-day average concentrations in standard farm pond for max rates.

Pond	Peak	4-day	21-day	60-day
Scenario	1-year in 10-year concentration (µg/L)			
NC Sweet Potato	2390	1640	762	353
FL strawberry	2370	1490	486	198
GA Pecans	2330	1670	663	318
CA lettuce	2010	1540	687	279
FL tomato	1850	1110	525	242
GA Onion W irrig	1680	1130	479	223
FL citrus	1640	864	359	194
PA tomato	1310	935	481	224
TN nursery	1270	1020	556	332
NJ nursery	1260	1140	1050	847
PA apple	1120	792	448	194
CA almond W irrig	1090	695	314	173
PA apple	991	657	403	226
MI beans	986	605	266	139
ME potato	910	696	359	168
MI nursery	872	833	756	633
ND canola	809	470	222	114
OR Xmas Tree	709	456	277	189
FL nursery	697	448	219	177
OR nursery	663	466	303	191
CA nursery	581	390	224	150
CA onion W irrig	558	412	192	102
CA grapes W irrig	541	461	232	113
OR filberts	508	377	254	168
CA citrus W irrig	413	290	158	101
OR filberts	408	318	196	109
OR mint	398	307	226	149
IDN potato W irrig	363	271	198	140
PA turf	345	242	190	131
OR apple	339	258	215	153
ID potato W irrig	275	208	116	83.9
OR apple	221	163	137	71.3

Appendix 4. Representative Model Outputs

Surface Water Calculator (SWCC)
Summary of Water Modeling of d-limonene and the USEPA Standard Pond

Estimated Environmental Concentrations for d-limonene are presented in Table 1 for the USEPA standard pond with the NCSweetPotatoSTD field scenario. A graphical presentation of the year-to-year peaks is presented in Figure 1. These values were generated with the Surface Water Concentration Calculator (SWCC Version 1.106). Critical input values for the model are summarized in Tables 2 and 3.

This model estimates that about 1.2% of d-limonene applied to the field eventually reaches the water body. The main mechanism of transport from the field to the water body is by runoff (51.4% of the total transport), followed by erosion (34.5%) and spray drift (14.1%).

In the water body, pesticide dissipates with an effective water column half-life of 4.2 days. (This value does not include dissipation by transport to the benthic region; it includes only processes that result in removal of pesticide from the complete system.) The main source of dissipation in the water column is volatilization (effective average half-life = 4.3 days) followed by metabolism (119 days).

In the benthic region, pesticide is stable. The vast majority of the pesticide in the benthic region (99.29%) is sorbed to sediment rather than in the pore water.

Table 1. Estimated Environmental Concentrations (ppb) for d-limonene.

Peak (1-in-10 yr)	0.239E+04
4-day Avg (1-in-10 yr)	0.164E+04
21-day Avg (1-in-10 yr)	762.
60-day Avg (1-in-10 yr)	353.
365-day Avg (1-in-10 yr)	73.0
Entire Simulation Mean	42.2

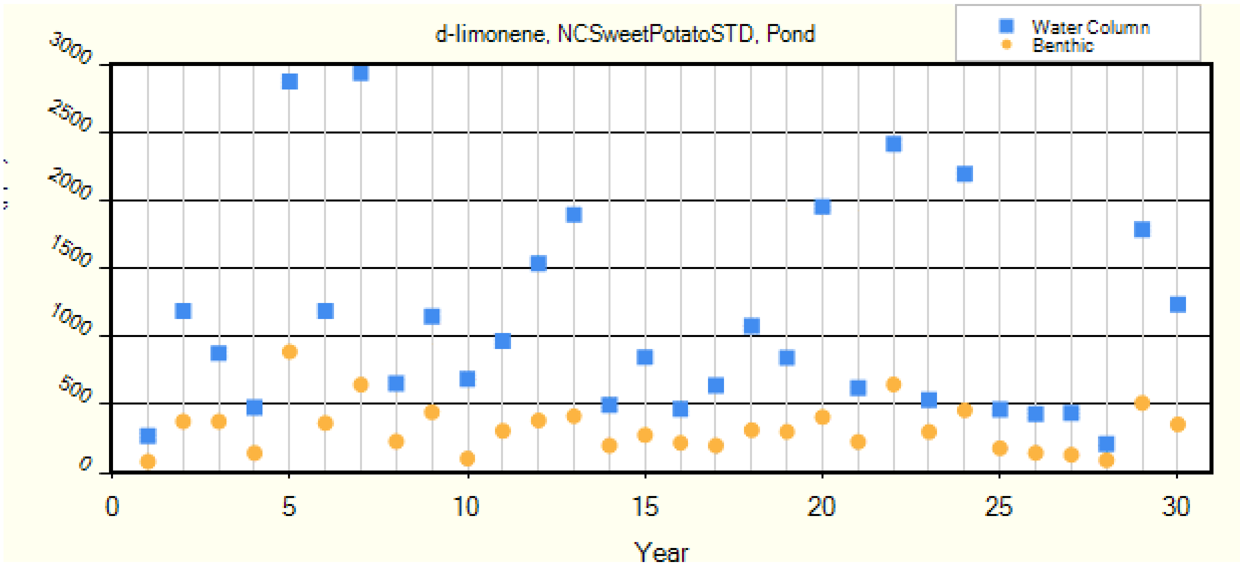
Table 2. Summary of Model Inputs for d-limonene.

Scenario	**NCSweetPotatoSTD**
Cropped Area Fraction	**1**
Koc (ml/g)	**1300**
Water Half-Life (days) @ 25 °C	**67.1**
Benthic Half-Life (days) @ 25 °C	**0**
Photolysis Half-Life (days) @ 28 °Lat	**0**
Hydrolysis Half-Life (days)	**0**
Soil Half-Life (days) @ 25 °C	**33**
Foliar Half-Life (days)	**0**
Molecular Wt	**136.23**
Vapor Pressure (torr)	**2**
Solubility (mg/l)	**13.8**

Table 3. Application Schedule for d-limonene.

Date (Days Since Emergence)	Type	Amount (kg/ha)	Eff.	Drift
1	Ground	38.75	0.99	0.017
3	Ground	38.75	.99	.017
5	Ground	38.75	.99	.017
7	Ground	38.75	.99	.017
9	Ground	38.75	.99	.017
11	Ground	38.75	.99	.017
13	Ground	38.75	.99	.017
15	Ground	38.75	.99	.017
17	Ground	38.75	.99	.017
19	Ground	38.75	.99	.017
21	Ground	38.75	.99	.017
23	Ground	38.75	.99	.017

Figure 1. Yearly Peak Concentrations



PRZM/EXAMS (PE5)
Without volatilization
stored as NJnurse.out
Chemical: d-limonene
PRZM environment: NJnurserySTD_V2.txtmodified Sunday, 30 September 2007 at 23:05:00
EXAMS environment: pond298.exvmodified Wedday, 15 November 2006 at 13:47:26
Metfile: w93730.dvfmodified Wedday, 3 July 2002 at 10:05:58
Water segment concentrations (ppb)

YearPeak96 hr21 Day60 Day90 DayYearly
196143041337526120855.58
196281664135117615742.45
196358256045035926670.93
196456541227314210428.34
196568750540023316844.49
1966201019201550810584156
196727721115713110730.14
19681650160014201040739195
196963460540720314438.24
197037930927815911130.31
197165348936830721757.74
197250937922313910628.75
1973130091837717912734.21
197416313711755.8145.6412.95
197553639826113799.326.98
197695874156031621858.29
1977125012201110534380100
19781930185015601170848225
197916501220667537395106
198052851146536026372.28
1981313330026716511732.31
198298894366135224965.93
198328224216492.5572.7421.59
198460057841423819452.56
198537529727215911030.61
19861660125055225018452.04
198788862754555400108
19885283262532823261.58
198924319914178.360.2116.84
199020215111059.3641.5912.22

Sorted results
Prob.Peak96 hr21 Day60 Day90 DayYearly
0.0322580645161292010192015601170848225
0.06451612903225811930185015501040739195
0.0967741935483871166016001420810584156
0.129032258064516165012501110555400108
0.16129032258064516501220754537395106
0.19354838709677413001220667534380100
0.225806451612903125094366136026672.28
0.25806451612903298891862535926370.93
0.290322580645161958886256035224965.93
0.3225806451612988883255232823261.58
0.35483870967741985274146531621858.29
0.38709677419354881664145030721757.74
0.41935483870967768760541426120855.58
0.45161290322580665357840725019452.56
0.48387096774193663456040023818452.04
0.51612903225806560051137723316844.49
0.54838709677419458250537520315742.45
0.58064516129032356548936817914438.24
0.61290322580645253641335117612734.21
0.64516129032258152841227816511732.31
0.6774193548387150939827315911130.61
0.70967741935483943037927215911030.31
0.74193548387096837930926714210730.14
0.77419354838709737530026113910628.75
0.80645161290322631329722313710428.34
0.83870967741935528224216413199.326.98
0.87096774193548427721115792.5572.7421.59
0.90322580645161324319914178.360.2116.84

0.935483870967742202151117 59.3645.6412.95
0.967741935483871163137110 55.8141.5912.22

0.1165915651389784.5565.6151.2
Average of yearly averages:62.2453333333333

Inputs generated by pe5.pl - Novemeber 2006
Data used for this run:
Output File: NJnurse
Metfile:w93730.dvf
PRZM scenario:NJnurserySTD_V2.txt
EXAMS environment file:pond298.exv
Chemical Name:d-limonene
DescriptionVariable NameValueUnitsComments
Molecular weightmwt136.23g/mol
Henry's Law Const.henry2.6e-2atm-m^3/mol
Vapor Pressurevapr2torr
Solubilitysol13.8mg/L
KdKdmg/L
KocKoc1300mg/L
Photolysis half-lifekdp0daysHalf-life
Aerobic Aquatic Metabolismkbacw67.1daysHalfife
Anaerobic Aquatic Metabolismkbacs0daysHalfife
Aerobic Soil Metabolismasm33.53daysHalfife
Hydrolysis:pH 70daysHalf-life
Method:CAM1integerSee PRZM manual
Incorporation Depth:DEPIcm
Application Rate:TAPP38.75kg/ha
Application Efficiency:APPEFF0.99fraction
Spray DriftDRFT0.017fraction of application rate applied to pond
Application DateDate01-01dd/mm or dd/mmm or dd-mm or dd-mmm
Interval 1interval2daysSet to 0 or delete line for single app.
app. rate 1apprate38.75kg/ha
Interval 2interval2daysSet to 0 or delete line for single app.
app. rate 2apprate38.75kg/ha
Interval 3interval2daysSet to 0 or delete line for single app.
app. rate 3apprate38.75kg/ha
Interval 4interval2daysSet to 0 or delete line for single app.
app. rate 4apprate38.75kg/ha
Interval 5interval2daysSet to 0 or delete line for single app.
app. rate 5apprate38.75kg/ha
Interval 6interval2daysSet to 0 or delete line for single app.
app. rate 6apprate38.75kg/ha
Interval 7interval2daysSet to 0 or delete line for single app.
app. rate 7apprate38.75kg/ha
Interval 8interval2daysSet to 0 or delete line for single app.
app. rate 8apprate38.75kg/ha
Interval 9interval2daysSet to 0 or delete line for single app.
app. rate 9apprate38.75kg/ha
Interval 10interval2daysSet to 0 or delete line for single app.
app. rate 10apprate38.75kg/ha
Interval 11interval2daysSet to 0 or delete line for single app.
app. rate 11apprate38.75kg/ha
Record 17:FILTRA
IPSCND1
UPTKF
Record 18:PLVKRT
PLDKRT
FEXTRC0.5
Flag for Index Res. RunIREPA Pond
Flag for runoff calc.RUNOFFnonenone, monthly or total(average of entire run)

PRZM/EXAMS (PE5)
With Volatilization
Diffusion In Air Coefficient DAIR = 4300 cm^2/day
Enthalpy of Vaporizaton = 10.48 kcal/mole

stored as NJnurseV.out
Chemical: d-limonene
PRZM environment: NJnurserySTD_V2.txtmodified Sunday, 30 September 2007 at 23:05:00
EXAMS environment: pond298.exvmodified Wedday, 15 November 2006 at 13:47:26
Metfile: w93730.dvfmodified Wedday, 3 July 2002 at 10:05:58
Water segment concentrations (ppb)

```
YearPeak96 hr21 Day60 Day90 DayYearly
196132531127214710226.56
196212711010049.0633.748.762
196331029626520614838.9
196410684.7576.4435.1224.16.27
196530929725512988.5823.06
196631330026720915039.45
196712911297.459.6143.1411.36
196832030627421415239.79
196931630225712484.6721.89
197030929525512888.4122.98
197131530226213894.8624.73
197212510894.6746.431.768.227
197312010390.3143.4529.727.693
197412310693.0144.5530.377.842
197511798.1987.3841.2528.237.309
197631730426413794.5124.67
197731930526513793.8724.44
197833932729422816443.44
197913811487.8451.5836.99.693
198031430026921015039.7
198131129725713794.5724.67
198232431026514197.4925.52
198313011298.2248.633.48.721
198430929725613391.8723.94
198530929525513592.7124.18
198612410794.1647.1232.58.508
198731830527221115240.09
198831530226013794.7924.7
198912911297.9248.2533.258.687
199012010390.743.7230.037.813

Sorted results
Prob.Peak96 hr21 Day60 Day90 DayYearly
0.032258064516129339327294228164443.44
0.064516129032258132531127421415240.09
0.096774193548387132431027221115239.79
0.12903225806451632030627221015039.7
0.16129032258064531930526920915039.45
0.19354838709677431830526720614838.9
0.22580645161290331730426514710226.56
0.25806451612903231630226514197.4925.52
0.29032258064516131530226513894.8624.73
0.32258064516129315302264137 94.7924.7
0.35483870967741931430026213794.5724.67
0.38709677419354831330026013794.5124.67
0.41935483870967731129725713793.8724.44
0.45161290322580631029725713592.7124.18
0.48387096774193630929725613391.8723.94
0.51612903225806530929625512988.5823.06
0.54838709677419430929525512888.4122.98
0.58064516129032330929525512484.6721.89
0.61290322580645213811410059.6143.1411.36
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0.67741935483871129112 97.9249.0633.748.762
0.70967741935483912911297.448.633.48.721
0.74193548387096812711094.6748.2533.258.687
0.77419354838709712510894.1647.1232.58.508
0.80645161290322612410793.0146.431.768.227
0.83870967741935512310690.744.5530.377.842
0.87096774193548412010390.3143.7230.037.813
0.90322580645161312010387.8443.4529.727.693
0.93548387096774211798.1987.3841.2528.237.309
0.96774193548387110684.7576.4435.1224.16.27

0.1323.6309.6272210.9151.839.781
 Average of yearly averages:21.1198333333333

Inputs generated by pe5.pl - Novemeber 2006
```

```
Data used for this run:
Output File: NJnurseV
Metfile:w93730.dvf
PRZM scenario:NJnurserySTD_V2.txt
EXAMS environment file:pond298.exv
Chemical Name:d-limonene
DescriptionVariable NameValueUnitsComments
Molecular weightmwt136.23g/mol
Henry's Law Const.henry2.6e-2atm-m^3/mol
Vapor Pressurevapr2torr
Solubilitysol13.8mg/L
KdKdmg/L
KocKoc1300mg/L
Photolysis half-lifekdp0daysHalf-life
Aerobic Aquatic Metabolismkbacw67.1daysHalfife
Anaerobic Aquatic Metabolismkbacs0daysHalfife
Aerobic Soil Metabolismasm33.53daysHalfife
Hydrolysis:pH 70daysHalf-life
Method:CAM1integerSee PRZM manual
Incorporation Depth:DEPIcm
Application Rate:TAPP38.75kg/ha
Application Efficiency:APPEFF0.99fraction
Spray DriftDRFT0.017fraction of application rate applied to pond
Application DateDate01-01dd/mm or dd/mmm or dd-mm or dd-mmm
Interval 1interval2daysSet to 0 or delete line for single app.
app. rate 1apprate38.75kg/ha
Interval 2interval2daysSet to 0 or delete line for single app.
app. rate 2apprate38.75kg/ha
Interval 3interval2daysSet to 0 or delete line for single app.
app. rate 3apprate38.75kg/ha
Interval 4interval2daysSet to 0 or delete line for single app.
app. rate 4apprate38.75kg/ha
Interval 5interval2daysSet to 0 or delete line for single app.
app. rate 5apprate38.75kg/ha
Interval 6interval2daysSet to 0 or delete line for single app.
app. rate 6apprate38.75kg/ha
Interval 7interval2daysSet to 0 or delete line for single app.
app. rate 7apprate38.75kg/ha
Interval 8interval2daysSet to 0 or delete line for single app.
app. rate 8apprate38.75kg/ha
Interval 9interval2daysSet to 0 or delete line for single app.
app. rate 9apprate38.75kg/ha
Interval 10interval2daysSet to 0 or delete line for single app.
app. rate 10apprate38.75kg/ha
Interval 11interval2daysSet to 0 or delete line for single app.
app. rate 11apprate38.75kg/ha
Record 17:FILTRA
 IPSCND1
 UPTKF
Record 18:PLVKRT
 PLDKRT
 FEXTRC0.5
Flag for Index Res. RunIREPA Pond
Flag for runoff calc.RUNOFFnonenone, monthly or total(average of entire run)
```

Appendix 5. TREX Model Sample Input/Output

INPUT

Table 1. Input- Orange Guard (4.6 lb a.i./A)

Chemical Name:	d-limonene	
Use	0	
Formulation	Orange Guard	
Application Rate	4.6	lb a.i./acre
Half-life	35	days
Application Interval	7	days
Maximum # Apps./Year	6	
Length of Simulation	1	year
Variable application rates?	no	

Endpoints			
Avian	Bobwhite quail	LD50 (mg/kg-bw)	0.00
	Bobwhite quail	LC50 (mg/kg-diet)	5600.00
	Mallard duck	NOAEL(mg/kg-bw)	0.00
	Bobwhite quail	NOAEC (mg/kg-diet)	0.00
Mammals		LD50 (mg/kg-bw)	4400.00
		LC50 (mg/kg-diet)	0.00
		NOAEL (mg/kg-bw)	250.00
		NOAEC (mg/kg-diet)	5000.00

Output

Table 2. Upper Bound Kenaga, Subacute Avian Dietary Based Risk Quotients- Orange Guard (4.6 lb a.i./A) (For Characterization-non-definitive endpoint)

	EECs and RQs									
	Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/ Seeds		Arthropods	
LC50	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ
5600	4816.21	0.86	2207.43	0.39	2709.12	0.48	301.01	0.05	1886.35	0.34

Table 3. Upper Bound Kenaga, Acute Mammalian Dose-Based Risk Quotients - Orange Guard (4.6 lb a.i./A)														
Size Class (grams)	Adjusted LD50	EECs and RQs												
		Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/ Seeds		Arthropods		Granivore		
		EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	
15	9670	4592	0.47	2105	0.22	2583	0.27	287	0.03	1798	0.19	64	0.01	
35	7824	3174	0.41	1455	0.19	1785	0.23	198	0.03	1243	0.16	44	0.01	
1000	3384	736	0.22	337	0.10	414	0.12	46	0.01	288	0.09	10	0.00	

Table 4. Upper Bound Kenaga, Chronic Mammalian Dose-Based Risk Quotients- Orange Guard (4.6 lb a.i./A)													
Size Class (g)	Adjusted NOAEL	EECs and RQs											
		Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/ Seeds		Arthropods		Granivore	
		EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ
15	549.5	4592	8.36	2105	3.83	2583	4.70	287	0.52	1798	3.27	64	0.12
35	444.6	3174	7.14	1455	3.27	1785	4.02	198	0.45	1243	2.80	44	0.10
1000	192.3	736	3.83	337	1.75	414	2.15	46	0.24	288	1.50	10	0.05

Input

Table 5. Input- Orange Guard (4.6 lb a.i./A with 2 day foliar dissipation half-life)

Chemical Name:	d-limonene	
Use	0	
Formulation	Orange Guard	
Application Rate	4.6	lb a.i./acre
Half-life	2	days
Application Interval	7	days
Maximum # Apps./Year	6	
Length of Simulation	1	year
Variable application rates?	no	

Endpoints			
Avian	Bobwhite quail	LD50 (mg/kg-bw)	0.00
	Bobwhite quail	LC50 (mg/kg-diet)	5600.00
	Mallard duck	NOAEL(mg/kg-bw)	0.00
	Bobwhite quail	NOAEC (mg/kg-diet)	0.00
Mammals		LD50 (mg/kg-bw)	4400.00
		LC50 (mg/kg-diet)	0.00
		NOAEL (mg/kg-bw)	250.00
		NOAEC (mg/kg-diet)	5000.00

Table 6. Upper Bound Kenaga, Subacute Avian Dietary Based Risk Quotients- (4.6 lb a.i./A-2-day for characterization)										
	EECs and RQs									
	Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/Seeds		Arthropods	
LC50	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ
5600	1211.04	0.22	555.06	0.10	681.21	0.12	75.69	0.01	474.32	0.08

Table 7. Upper Bound Kenaga, Acute Mammalian Dose-Based Risk Quotients (4.6 lb a.i./A-2-day for characterization)													
Size Class (grams)	Adj. LD50	EECs and RQs											
		Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/ Seeds		Arthropods		Granivore	
		EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ
15	9670	1155	0.12	529	0.05	649	0.07	72	0.01	452	0.05	16	0.002
35	7824	798	0.10	366	0.05	449	0.06	50	0.01	313	0.04	11	0.001
1000	3384	185	0.05	85	0.03	104	0.03	12	0.00	72	0.02	3	0.001

Table 8. Upper Bound Kenaga, Chronic Mammalian Dose-Based Risk Quotients (4.6 lb a.i./A-2-day for characterization)													
Size Class (grams)	Adjusted NOAEL	EECs and RQs											
		Short Grass		Tall Grass		Broadleaf Plants		Fruits/Pods/ Seeds		Arthropods		Granivore	
		EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ	EEC	RQ
15	549	1155	2.10	529	0.96	649	1.18	72	0.13	452	0.82	16	0.03
35	445	798	1.80	366	0.82	449	1.01	50	0.11	313	0.70	11	0.02
1000	192	185	0.96	85	0.44	104	0.54	12	0.06	72	0.38	3	0.01

Appendix 6. Terr Plant Model Input/output

Table 1. Chemical Identity.	
Chemical Name	Limonene
Use	Christmas tree plantation
Application Method	Ground
Application Form	Spray
Solubility in Water (ppm)	13

Table 2. Input parameters used to derive EECs.

Input Parameter	Symbol	Value	Units
Application Rate	A	55.2	Lb/A
Incorporation	I	1	none
Runoff Fraction	R	0.02	none
Drift Fraction	D	0.01	none

Table 3. EECs for Limonene. Units in lb /A.

Description		EEC
Runoff to dry areas	(A/I)*R	1.104
Runoff to semi-aquatic areas	(A/I)*R*10	11.04
Spray drift	A*D	0.552
Total for dry areas	((A/I)*R)+(A*D)	1.656
Total for semi-aquatic areas	((A/I)*R*10)+(A*D)	11.592

Table 4. Plant survival and growth data used for RQ derivation. Units are in lb /A.

	Seedling Emergence		Vegetative Vigor	
Plant type	EC25	NOAEC	EC25	NOAEC
Monocot	x	x	2.83	0.19
Dicot	x	x	7.09	1.31

Table 5. RQ values for plants in dry and semi-aquatic areas exposed to Limonene through runoff and/or spray drift.*

Plant Type	Listed Status	Spray Drift
Monocot	non-listed	0.20
Monocot	listed	2.91
Dicot	non-listed	<0.1
Dicot	listed	0.42

Table 6. Chemical Identity.	
Chemical Name	Limonene
Use	Variety of Ag Crops-Burndown
Application Method	Ground
Application Form	Spray
Solubility in Water (ppm)	13

Table 7. Input parameters used to derive EECs.			
Input Parameter	Symbol	Value	Units
Application Rate	A	34.6	lb/A
Incorporation	I	1	none
Runoff Fraction	R	0.02	none
Drift Fraction	D	0.01	none

Table 8. EECs for Limonene. Units in lb/A.		
Description	Equation	EEC
Runoff to dry areas	(A/I)*R	0.692
Runoff to semi-aquatic areas	(A/I)*R*10	6.92
Spray drift	A*D	0.346
Total for dry areas	((A/I)*R)+(A*D)	1.038
Total for semi-aquatic areas	((A/I)*R*10)+(A*D)	7.266

Table 9. Plant survival and growth data used for RQ derivation. Units are in lb/A.				
	Seedling Emergence		Vegetative Vigor	
Plant type	EC25	NOAEC	EC25	NOAEC
Monocot	x	x	2.83	0.19
Dicot	x	x	7.09	1.31

Table 10. RQ values for plants in dry and semi-aquatic areas exposed to Limonene through runoff and/or spray drift.*				
Plant Type	Listed Status	Dry	Semi-Aquatic	Spray Drift
Monocot	non-listed	#VALUE!	#VALUE!	0.12
Monocot	listed	#VALUE!	#VALUE!	1.82
Dicot	non-listed	#VALUE!	#VALUE!	<0.1
Dicot	listed	#VALUE!	#VALUE!	0.26

*If RQ > 1.0, the LOC is exceeded, resulting in potential for risk to that plant group.

Table 11. Chemical Identity.	
Chemical Name	Limonene
Use	Vine Crops
Application Method	Ground
Application Form	Spray
Solubility in Water (ppm)	13

Table 12. Input parameters used to derive EECs.

Input Parameter	Symbol	Value	Units
Application Rate	A	18.4	lb/A
Incorporation	I	1	none
Runoff Fraction	R	0.02	none
Drift Fraction	D	0.01	none

Table 13. EECs for Limonene. Units in lb/A.

Description	Equation	EEC
Runoff to dry areas	(A/I)*R	0.368
Runoff to semi-aquatic areas	(A/I)*R*10	3.68
Spray drift	A*D	0.184
Total for dry areas	((A/I)*R)+(A*D)	0.552
Total for semi-aquatic areas	((A/I)*R*10)+(A*D)	3.864

Table 14. Plant survival and growth data used for RQ derivation. Units are in lb/A.

	Seedling Emergence		Vegetative Vigor	
Plant type	EC25	NOAEC	EC25	NOAEC
Monocot	x	x	2.83	0.19
Dicot	x	x	7.09	1.31

Table 15. RQ values for plants in dry and semi-aquatic areas exposed to Limonene through runoff and/or spray drift.*

Plant Type	Listed Status	Dry	Semi-Aquatic	Spray Drift
Monocot	non-listed	#VALUE!	#VALUE!	<0.1
Monocot	listed	#VALUE!	#VALUE!	0.97
Dicot	non-listed	#VALUE!	#VALUE!	<0.1
Dicot	listed	#VALUE!	#VALUE!	0.14

Appendix 7. Sample Input/output for Ag Drift Analysis
(Examples entered for listed Monocots)

Table 1. Avenger Label-Medium-Course Droplet (34.6 lb a.i./A)

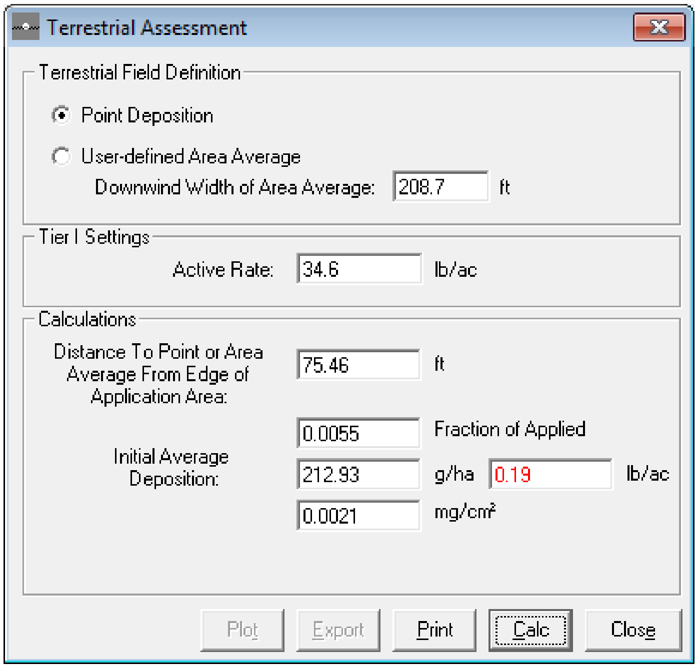


Table 2. Orange Guard Label- Fine to Very Fine Droplet (4.6 lb a.i./A)

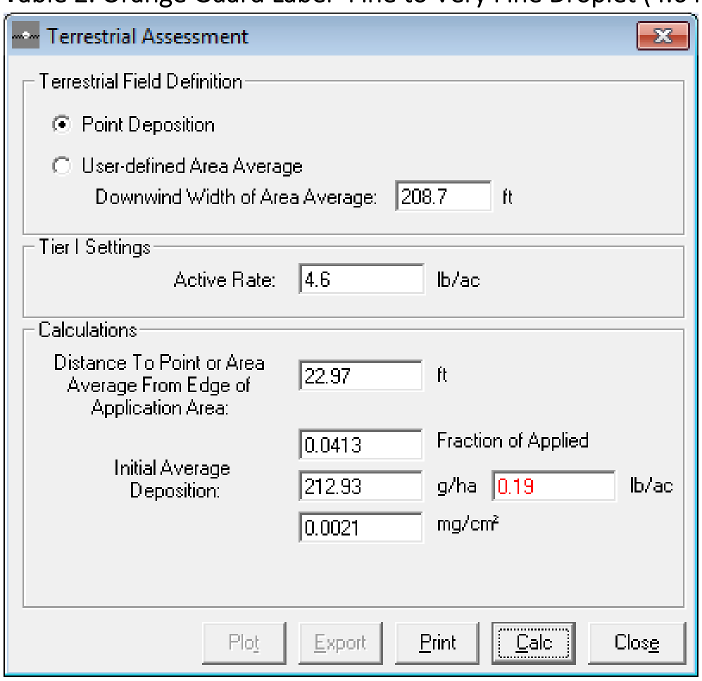


Table 3. Orange Guard Label- Fine to Very Fine Droplet (18.4 lb a.i./A)

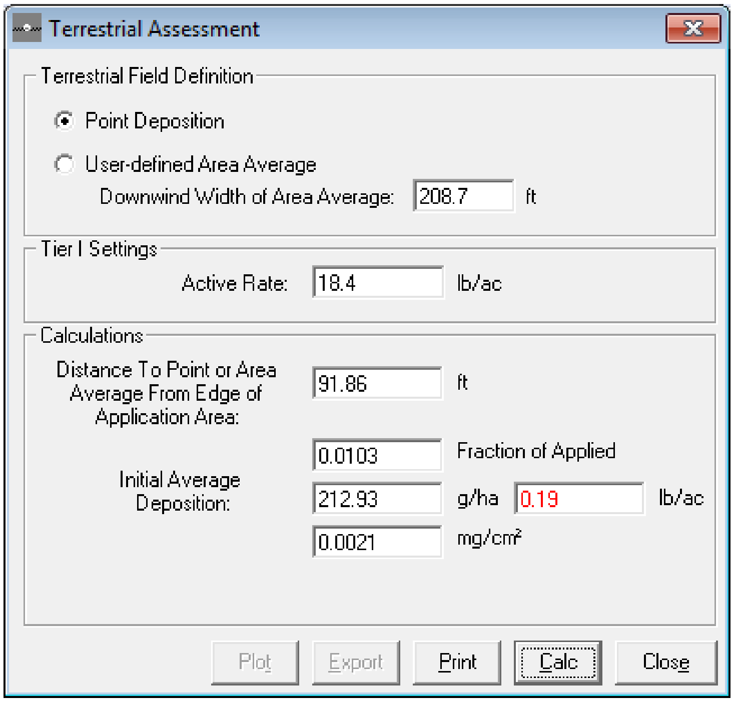
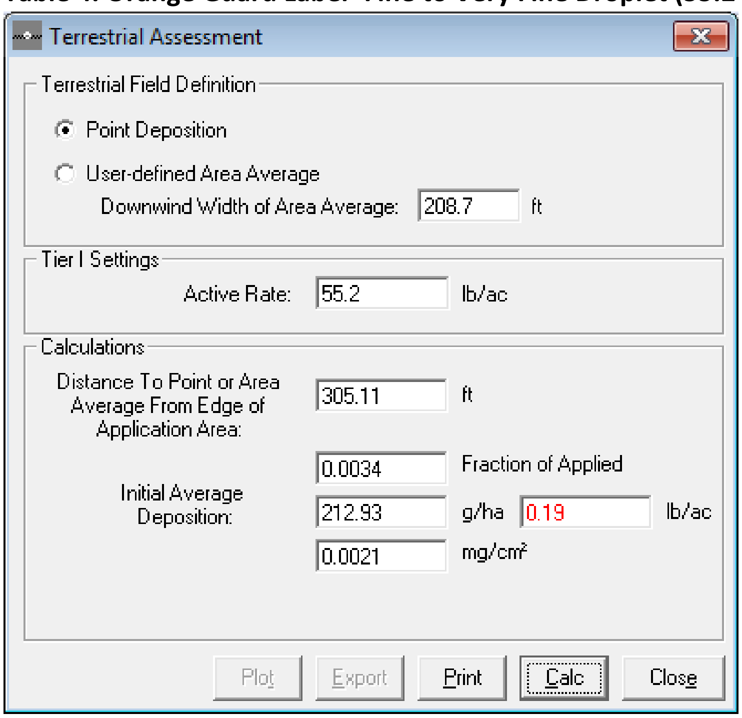


Table 4. Orange Guard Label- Fine to Very Fine Droplet (55.2 lb a.i./A)



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